CORROSION OF COPPER IN A PUBLIC WATER SUPPLY

BY

Javed Akhtar

Thesis submitted for the degree of Master of science
to the Faculty of Engineering

Department of Mechanical Engineering
University of Glasgow

July, 1989

To,

My Parents

CONTENTS

ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. Trevor Hodgkiess for his invaluable help and critical supervision throughout this work.

I am indebted to Mr. Ian Stewart and Dr. Liz Macdonnel for their assistance and valuable discussion.

I would like to thank Mr. Andy Ramasay and Mr. Niel Flaherty for their help in the equipment and photographic section.

I am also indebted to the staff and colleagues, past and present for their help in various ways.

My special thanks to FATA, Govt. of N.W.F.P. Pakistan who fully financed my studies.

Finally, Special thanks to my family especially to my wife for their constant support and encouragement througout this work.

ABSTRACT

This work has involved an initial investigation into the extent and causes of copper corrosion in Glasgow tapwater.

The literature has been surveyed to obtain information on the behaviour of copper in waters of widely varying composition in various parts of the world.

Experiments have been carried out in which copper specimens have been exposed to Glasgow tapwater, for periods of upto one year,to a variety of conditions involving stagnant and slowly-flowing water, temperature from ambient to 60°C, aerated and de-aerated water. Additionally, a small amount of work was devoted to investigations of the pH stability of Glasgow water, to the effect of illumination on the corrosion behaviour and also to a comparison of corrosion behaviour in Glasgow tapwater with water from another locality.

Modification to the existing electrochemical equipments and techniques have been made to enable electrochemical experiments to be carried out in the range of conditions in the low conductivity water characteristics of this locality. The electrochemical corrosion behaviour of several grades of copper have been studied in different environmental conditions.

It was found that in slowly moving cold water the copper specimens appear to develop a protective film and therefore indicating satisfactotry performance of copper in this situation for the periods of time involved in this work.

Similar protective film behaviour was observed for copper specimens in slowly moving hot water (40-50°C) and also in rapidly moving hot water after some time. The results obtained from the flowing rig suggest the different behaviour for the same grade of copper obtained from different merchants.

In moving hot water at 60°C, the corrosion was more complex with copper specimens upon intial exposure, being clearly active and appearing to remain so for a period upto one year, despite the formation of an adherent thin corrosion product underneath a more powdery deposit. However, the corrosion rates estimated from Tafel extrapolation were low, especially after the first few days, thus indicating that the corrosion product was providing some corrosion protection but not by the classic passive-film mechanism exhibited at the lower temperatures. There was some visual evidence of the onset of localised pitting after about one year exposure at 60°C. The results in hot water at 60°C suggest that the performance of copper may be less satisfactory in this condition. The observed findings are discussed in terms of their relevance to the practical problems experinced.

CHAPTER I

INTRODUCTION

Copper is used world wide for fresh water installation such as pipes for cold and hot water, water heaters and boilers. It generally gives reliable performance and has a long life. However, corrosion problems in copper plumbing systems are sometimes encountered and historically, these have tended to have been in soft water regions of the world. Other factors, which have been found to be associated with corrosion problems in such systems, have been velocity (causing erosion corrosion), installation procedures (Flux related corrosion problems) and surface condition of the copper pipe work. For instance, there was an outbreak of corrosion problems, some time ago, caused by carbon residues (1) remaining on the tube after manufacturing but this is now avoidable by taking suitable measures.

The analysis made in Japan (2) has also been shown that both pitting and erosion corrosion were regarded as the predominent cause of failures. The erosion corrosion can be avoided either by decreasing the water velocity or by changing the system design, but pitting corrosion can be much more complex in origin.

It is widely accepted that pitting corrosion of copper tube can be classified into several types depending on pit morphology, corrosion products and water in which it occurs.

The failure mode can be rapid under the conditions studied by Gentil (3). In his work several factors were involved.

The first factor was the excessive water velocity which cause erosion corrosion or impingement attack.

The second factor was related to carbon dioxide because in soft waters high in CO_2 tend not to form a protective film inside the copper tube.

The third factor was the combination of this high CO_2 with the dissolved oxygen to stimulate the pitting process and can produce early failures of the tubes. Some of the factors which take part in the corrosion process has also been studied by the Cornwell and his colleagues (4).

The presence of organic inhibitor in the surface derived has been discussed by Campbell (5) in his work but these are removed after the treatment process.

In the last five years or so there has been an increasing incidence of pitting corrosion failures of copper plumbing system in Scotland and especially in the west of Scotland. The problem first arose in hospitals and is so wide spread that more seems to be scarcely any hospital in the west of Scotland which are unaffected, entire hot water and cold water systems are having to be replaced and costs of millions of pounds per hospital.

A recent survey carried out in the course of a final year (6) undergraduate project in this department revealed that a significant proportions of large hotels have suffered similar problems and there have also been instances of pris ons and schools being similarly affected. Photographs of copper pipe from local hospital and a hotel are shown in figures 1-3.

A major concern currently is that the cause of these corrosion problems is unknown despite, a number of examination and surveys of tube material which have been carried out. Consequently, some consideration is being given to the alternative use of U-PVC tubing especially for cold system. However most of the replacement systems , especially in hot water system are in copper and this lack of understanding of the cause of corrosion leads to considerable concern about the future performance of such system.

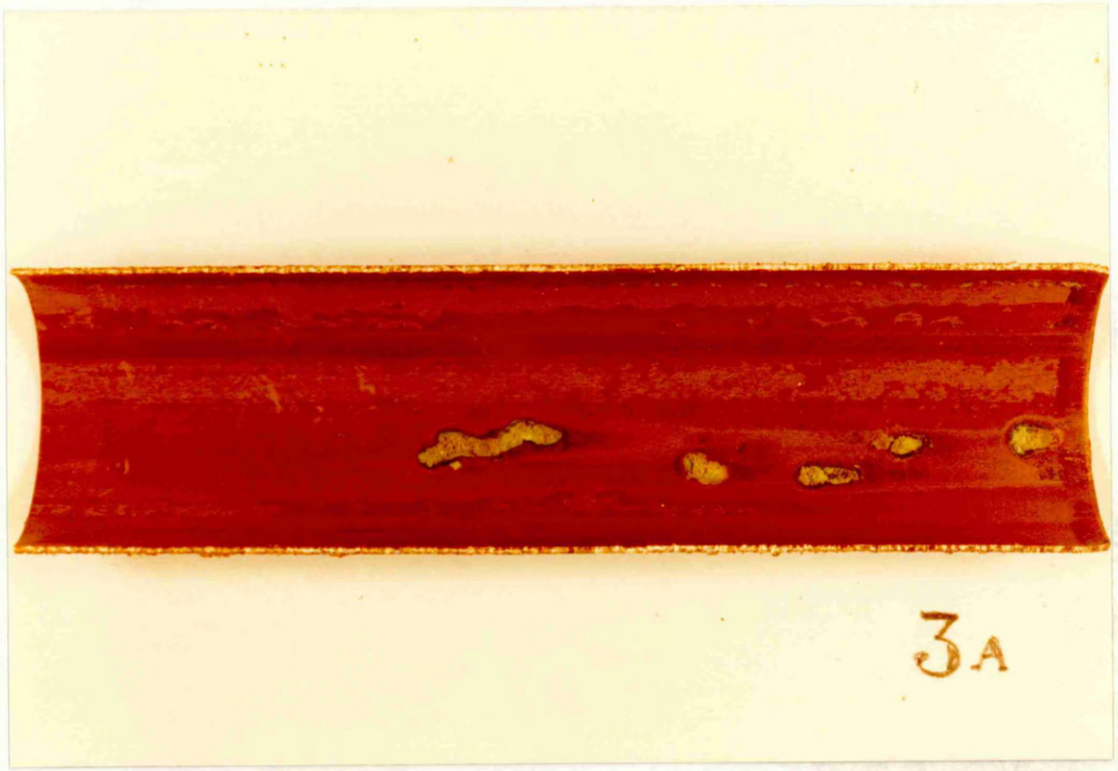
Copper tubes used in the building industry for domestic water services should be manufactured to BS 2871(7). The part 1 of BS 2871 covers the specification of tubes designated for water, gas and sanitation purposes.

Several grades of copper specimens have been used in this experimental work. These grades are called B1,B2,B3 and B4. The grade B1 represents the copper specimens made from old copper tube (sample) obtained from a hotel.

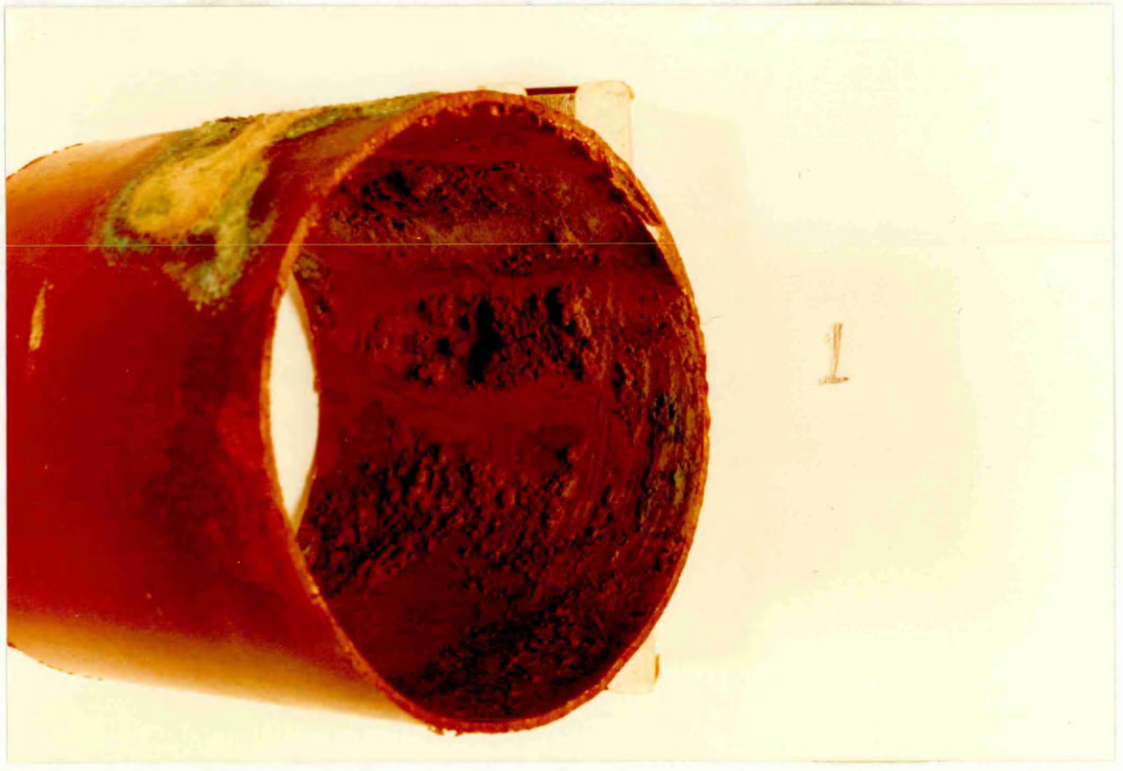
The grade B2 represents the copper specimens made from new copper [BS 2871] obtained from a stockist. This copper has only been used in the comparison of Glasgow water verses Lancashire water experimental work.

The specimens made from the other two grades of copper which is called B3 and B4 has been discussed in more detail later in chapter 3 in accordance with the British standered.

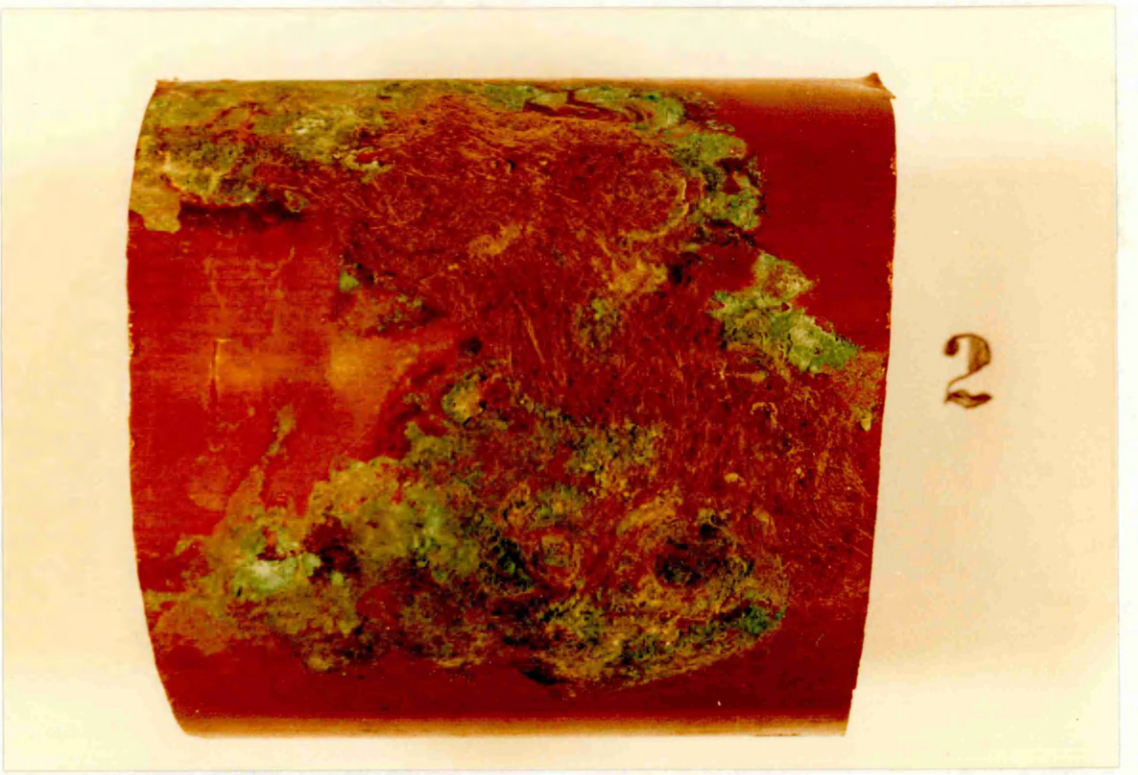
It is worthwhile to point out that B1 and B3 copper has been used most often in all the experiments while the other two grades has rarely been used.



Photograph 1 shows the onset of corrosion in form of isolated pits on the interior surface(pipe)



Photograph 2 shows more extensive corrosion product in a pipe bore.



Photograph 3 shows the spread of corrosion product to outside of a pipe after perforation.

CHAPTER II

LITERATURE REVIEW

2.1.1. CORROSION

Corrosion may be defined as the deterioration of a substance (usually a metal) or its properties because of its reaction with the surrounding environment. In the corrosion reaction the metal itself is oxidised to a higher valency state while the other reactant is reduced to a lower valency state. In the electrochemical reaction in which one metal is oxidised and the other one is reduced produce the formation of compounds called corrosion products.

The most desirable classification of corrosion is the dry and wet corrosion. Dry corrosion is usually associated with high temperature while wet corrosion occurs when a liquid is present. The corrosion characteristic of a metal is not an inherent property and both the nature and rate of corrosion will depend upon the exposed environment.

Almost all metals are unstable because the production of metals contains extracting the metal out from their ores which raise their free energy and also provides a tendency for the metal in most environments to react with other elements and can lower their free energy(8).

Corrosion may takes many forms depending on the metals and the exposed environments and the corrosion process by which damage is occuring.

Since metallic corrosion is almost always an electrochemical process, so it is possible to divide corrosion into anodic and cathodic reactions.

a: Anodic reaction : The electrode at which oxidation or corrosion occurs.

$$M \text{ ----> } M^{n+} + ne$$

In case of copper $Cu \text{ ----> } Cu^{2+} + 2e$

b: Cathodic reaction : The electrode where reduction (practically no corrosion) occurs.

The most common cathodic reactions encountered during the corrosion of metals are hydrogen evolution and oxygen reduction reactions.

Hydrogen evolution $2H^+ + 2e \text{ ----> } H_2$ (Gas)

Oxygen reduction $O_2 + 2H_2O + 4e \text{ ---> } 4\ OH^-$

General corrosion occurs when the anodic and cathodic reactions occur simultaneously over the entire surface. If the anodic and cathodic reactions are permanently separated then localised corrosion occurs at the anodic site.

The scope of this thesis is primarily limited to the pitting corrosion of copper. So pitting corrosion of copper will be discussed in more detail.

2.1.2. **PITTING CORROSION**

The electrochemical concept of corrosion in aqueous solutions requires that in any corrosion process the anodic and cathodic reactions must be faradically equal.

In general corrosion the anodic and cathodic sites migrate in a random manner over the surface of the metal as the process continues, but when different areas of the metal become anodic or cathodic, the corrosion localised at the anodic sites. since the anodic and cathodic currents are equal and a situation in which the anodic area is small in relation to the cathodic area can result intense local dissolution and rapid penetration of the metal.

Pitting corrosion is one of the most destructive and insidious forms of corrosion. Pits are somtimes isolated or so close togather that it looks like a rough surface.

It is very diffcult to detect pits because of their tiny nature and are also often covered with the corrosion products.

Pitting is also often very diffcult to predict by laboratory tests because sometimes the pits require a long time i.e. several months or years to show up in actual service. Pitting should be divided into two stages ie initiation and propagation.

According to the authors (9) and (10) the factors affecting the propagation stage of a pit are different from those that leads to its initiation.

In copper plumbing system Corrosion always takes place in the form of pitting corrosion. Pitting corrosion of copper in supply water may be conceived in a wide sense, and includes several forms of corrosion operating by apparently different mechanisms. Where copper is concerned the classical concept of pitting, a small anode surrounded by a large cathode appears often to be inappropriate. Its unusual behaviour is reflected also in what would be considered in other metals to be crevice corrosion or deposit attack.

In the pitting corrosion of copper there is dissolution of the metal at areas that are expected to be cathodic ie; Oxygen is readily available and not as in the expected cases at areas where access to dissolved oxygen is restricted. Several types of pitting corrosion of copper are recently recognised (11,12,13,14) and operating by apparently different mechanisms.

Type 1: This type of pitting attack is most commonly associated with hard or moderatly hard water. This type of attack is more likely to take place in cold water rather than hot water. This form of attack is most frequently recognised by the pit shape and structure. The pits are generally large, roughly hemispherical or saucer shape cavities containing cuprous chloride and oxide.

The pits are generally covered with precipitated $CaCO_3$ and basic copper carbonate forming a green or green blue nodule on the copper surface.

Type 2: This type of attack occurs in certain soft waters and rarely occurs when the water temperature is below 60^0C. This form of attack is identified by pit morphology which is usually narrow deep pits and containing hard crystalline cuprous oxide. These pits are sometimes covered with small dark brown or black nodules of corrosion products. Frequently no corrosion products are visible and the surface being covered with a fairly uniform black layer of mixed copper oxide.

Type 3: This form of attack is considered to be different from the other types and is comparatively recent phenomenon. This type of attack is recognised by the colour and composition of the corrosion products mound formed above the pits.

This corrosion product are more blue in colour than the green/blue corrosion products of type 1 pitting and contains substantial amounts of basic copper sulphate.

Type 4: This type of attack is relatively a rare form of corrosion. It appears not normally to produce penetration of the copper and complaints of water leakage. At the initial stage it takes the form of a large number of small pits distributed uniformly over the copper surface. These pits are filled with cuprous oxide corrosion product and grow very rapidly at the periphery to the extent where finaly join togather and are not then recognisable as corrosion pits in the normal accepted sense. This results in high copper contents in the water.

It is clear from the literature that the most common and significant form of failure is type 1 pitting corrosion. The type 2 pitting corrosion occurs only in certain soft water region of the world. Consequently the mechanism of type 1 pitting has been studied more extensively and is discussed below in more detail while the mechanism of type 2 pitting is unknown.

2.1.3. MECHANISM OF TYPE 1 PITTING CORROSION

The mechanism of pitting corrosion of copper was first studied in detail by May (15). He stressed on the important role of solid cuprous chloride within the pit which acts as a highly efficient oxygen screen, which means to prevent oxyg en in the water from reaching the bottom of the pit and the precipitation of sparingly soluble salt was considered important in keeping the copper ion concentration low and preventing the polarisation of the anode.

He also proposed different ways in which pit might be initiated by local breakdown or blistering of normally protective oxide films on the copper surface as a result of differential aeration cells set up by deposits.

Campbell (16) convinced by Mays view and he suggest that carbon film provides in the tube large effective cathodic areas, anodic dissolution occuring at discontinuities in the film where the copper is exposed.

Membrane cell theory was developed by Lucey (17) in 1967. This theory is based on the detailed examination of service failures and laboratory experiments. Before this it had been assumed that pitting corrosion was the result of large cathodic region surrounding a small anodic region. In the case of hard water the production of hydroxyl ions by the reduction of oxygen at cathodic area would cause precipitation of $CaCO_3$ on the cathode surface.

He found after the examination of copper pipes and tanks from hard water districts, that there was no more carbonate scale deposited around the pits than on other parts of the surface quite remote from any pitting. There was a large amount of $CaCO_3$ present in the mound immediately above the pit. This suggested that the reduction of dissolved Oxygen in water takes place immediatly above the pit and not on the surrounding surface. He also found that a thin cuprous oxide membrane is present across the mouth of the pit and this acts as a bipolar membrane electrode ie; the under surface is acting anodically while the upper suf ace is acting cathodically.

The cuprous chloride produced within the pit is anodically oxidised to cupric ions on the under surface of the oxide membrane and the cupric ions thus produced attack further copper within the pit to reform cuprous ions. The main cathodic process occuring on the upper surface of the oxide membrane is the reduction of cuprous ions by reaction with dissolved oxygen in the water. The cuprous ions for this reaction are provided partly by diffusion through pores in the oxide membrane from within the pit and partly by recycling of the cuprous ions produced by the cathodic reduction at the upper surface of the oxide membrane. A mound forms above the pit consists partly of basic cupric salts and partly of $CaCO_3$ which is formed by the reaction between the cuprous ions, oxygen and $CaCO_3$.

2.2.1. WATER CHEMISTRY

This plays an important role in the corrosion process. Special attention will be devoted to this aspect, since the current localised problem of copper corrosion in the west of Scotland might well be associated with some aspects of local water composition.

The quality of water entering a building depends on several factors which includes, the tract of land from which reservoirs obtain their supply, the treatment of water at the purification plants and the essentials and constructions of water distribution system which generally provide the water supply available to the consumers. At each stage the water adds or loose some constituents which may influence the corrosion rate of copper pipes.

Some features of the water chemistry that can affect the corrosion rate of copper are mentioned below.

2.2.2. WATER HARDNESS

The formation of protective film on copper is basically related to the environmental water chemistry.

During the 1975 there was a problem of unique nature in two places of Sweden . The investigation of the problem was carried out by Linder and Lindman (14). They identified the attack which was type 3 and the main cause of the problem was environmental acidification. The problem was completely eleminated by increasing the HCO_3^- concentration which is the major carbonate constituents of drinking water. The equilibrium established between the carbonate and sulphate corrosion products are as follows;

$$Cu_4SO_4(OH)_6 + 2HCO_3^- = 2Cu_2CO_3(OH)_2 + SO_4^{2-} + 2H_2O$$

(Brochantite) (Malachite)

This indicate that the presence of malachite as a corrosion product is more conducive to pitting corrosion resistance than brochantite. These examples are a practical development of the experimental work carried out by Mattsson and Fridriksson(18) in 1968.

They developed a corrosion cell with an anode in the capillary tube in which they examined the position of the corrosion products with the modification of the water.

Three position were identified ie crust at the end of the anode, crust outside the capillary and crust in the capillary away from the anode.

All these crusts corresponding to different environmental conditions ie free from $SO_4^{2-}$and Cl^- ions, water containing SO_4^{2-}ions and all SO_4^{2-} and Cl^- ions water with a high concentration of carbonate (280mg/L of HCO_3^-). Severe corrosion was observed in the water containing SO_4^{2-}ions where the corrosion product was observed outside the capillary as mentioned before.

The addition of sulphate ions or chloride ions not only influence the conductivity of the water but also the transport number of different ions, ie; the part of the current transported by different ions.

A tap water which has shown tendency to cause pitting can be made less corrosive by an increase in its pH value and HCO_3^- content.

The addition of sulphate reduces the supply of HCO^-_3 to the metal surface (because both HCO_3^- and SO_4^{2-} are arriving at metal surface.) and hence reduces the possibility of carbonate deposition and therefore increase copper dissolution. Their addition to water should be limited as much as possible. These condition should be observed during the aluminium sulphate flocculation stage in water purification.

2.2.3. pH

The most important factor is of course the chemical nature of the electrolyte in which the metal is corroding. At the same time an extremely important characteristics of the electrolyte is the value of pH of the electrolyte solution. The pH may be defined as the direct measure of the hydrogen ion concentration. Hydrogen evolution is the more favoured cathodic reaction at low pH values while Oxygen reduction becomes the predominent cathodic reaction at high pH values. Therefore consideration of the influence of the nature of the electrolyte upon the rate and distribution of the corrosion will start with the dependence of the corrosion rate upon pH of the solution.

The influence of pH has been mentioned by Akimov (19) for different metals. The pH of water also affect the corrosion rate of copper in a plumbing system.

Lucey (20,21) has suggested that several inorganic constituents (Cl^-, NO_3^-, SO_4^{2-}, Na^+) are important in determining the pitting propensity of a water but pH is also a major factor in the range of 7 to 9.4.

The effect of pH has also been studied by Mattsson and Fridriksson (18) and they have found that the pitting tendency is noticeably greater below pH 7 than above this value. The reason may be that at higher pH values a protective coating of corrosion products is formed which will sooner or later arrest the corrosion. Similar significance of pH has been observed by Cohen (22).

Watker (23) has reported on the Glasgow environs that generally raw water before treatment has a pH values in the range of 6.5 to 7.5 . These values are increase to 8 to 8.5 before entering the distribution system. The decline of PH during summer is also clear, ie; Seasonal inclination is also apparent, ie; pH declining during the autumn months. This may be due to the autumn turnover in the reservoirs and the seasonal deterioration in the quality of water.

2.2.4. ORGANIC INHIBITORS

It has been suggested that some waters tend to show resistance to pitting corrosion due to the presence of organic inhibtors as described by Campbell (16). Surface derived waters, ie; lake or river water do not give rise to pitting corrosion unless they have been given a flocculation treatment to remove these inhibitors. The role of the inhibitor is to modify the growth of the cuprous oxide.

In the absence of the inhibitor the oxide forms loose which affords no protection to the copper beneath it, while in its presence the oxide forms an adherent layers which prevents further corrosion.

2.2.5. RESIDUAL CHLORINE

This plays a great role in the corrosion of copper pipes in service. The residual chlorine is the chlorine involved in the sterilization treatment.

The disproportionation of chlorine gas or hypochlorite which is added to water for sterilisation produce hypochlorous acid (HOCl) and chlorite ions. The rate of this disproportionation reaction is also proportional to the temperature. The dissolved chlorine in water can lead to de-stabilisation of the developed protective film due to increase in electrode potential of the metal. Mattsson et al (18) has found that chloride ions not only affect the conductivity of the water but also increase the transport number of different ions.

The importance has been given to the effect of residual chlorine by many investigators from Japan. In the study carried out by Fujii et al (24,25) suggests that residual chlorine plays an important role in raising the potential of copper upto the critical value. They have also stated that pitting did not occur in water free of residual chlorine even under air saturated conditions.

In the investigation of Fujii et al (25) which was carried out in flowing synthetic water with and without the addition of oxidising agents such as dissolved oxygen and residual chlorine. They found that dissolved oxygen could not bring the potential of copper above the critical potential value but residual chlorine is responsible for such situation.

In the study carried out by suzuki et al (26,27) was a forward step to indicate the attack of chlorite (ClO^-_2) ions on the developed corrosion product layer on copper. The presence of residual chlorine increase the developed layer porosity because it increase the corrosion rate,

$$Cu_2O + 2ClO_2^- + H_2O = 2\ CuClO_2 + 2\ OH^-$$

Generally the metallic oxide layer has the ability to exchange anions and concentrate them in its pores. The chlorite comes from the bulk water into the corrosion layer and exchange with hydroxyl ions.

The mechanism of potential rise during the incubation period was studied by Suzuki et al (26,27). They conclude that the potential rise takes place in two stages. The first stage is the formation of Cu_2O layer in a certain range of potential while the second stage is the reaction of chlorite ions accumulated in the cuprous oxide layer.

In the study of Atlas et al (28) which demonstrate that free chlorine is the oxidising agent chiefly responsible for the corrosion of copper in chlorinated domestic water while the dissolved oxygen plays a comparatively minor role.

It is also recomended that the pH of the water should be adjusted after chlorination which markedly reduces the rate and extent of copper corrosion.

2.3.1. SYSTEM DESIGN/COMMISSIONING FACTORS

The system design has a great influence on the corrosion of copper pipes in service. A problem can arise due to excessive water velocities which in extreme condition can cause premature failure by one of several mechanism including erosion corrosion or cavitation attack which damage the developed protective film. The fluid flow dynamics has been studied by Campbell(29).

Such damage could occur in the poorly designed bends, coupling and in a situation where the tube diameter is not in accordance with the normal water velocity. For instance, a pipe of a small diameter with a high flow rate could be avoidable because this cause to damage the developed film on the pipe surface.

Also the non uniform hydrodynamic behaviour within copper pipes has been studied by Evans (30) which leads to the formation of concentration cells. He studied the influence of differential aeration on the corrosion of metals. In two tests electrode were immersed in the two-compartment cell with potassium chloride electrolyte and aerated copper became anodic due to the removal of an accumulation of copper ions from the metallic surface alters the potential in the negative direction. The current produced flowed in the opposite direction as compared to other metals because in the case of copper the current was flowing from the aerated to unaerated electrode. He demonstrate that this due to the formation of a concentration cell.

There is also a possibility of corrosion occuring in pipe work running only partially filled. Specially in large and complex installation it is important to avoid stagnant and semi stagnant condition prevails for long periods. The role of flow dynamics on film damage due to the debris must not be ignored.

The possibility of mechanical damage could exist where silicious materials and loose corrosion deposits erode. This aspect would be particularly aggressive in turbulent flow condition at inhomogenities in the pipe. The stagnant flow conditions promote the deposition of such materials and therefore the formation of differential aeration cells.

Manganese dioxide deposits have been associated with this problem(31).

This is also worthwhile that cold water service should be installed in such a way to avoid undue pick-up of heat from adjacent hot water pipes(32).

Also dead legs in plumbing system might well be a factor in the corrosion behavior of copper pipes as well as system temperature.

All the systems should be throughly flushed out as soon as possible after installation to remove the foreign matter.

It is also important to ensure that all the open pipes ends are correctly fitted with temporary caps at all the times during construction.

The use of shock doses of high chlorine water during commissioning in large buildings may have a long term affect on the corrosion or might also the condition of the system during possibly lengthly period between installation and commissioning and the actual use of the buildings.

2.4.1. METALLURGICAL FACTORS

Metallurgy and surface condition of copper also have influence on the pitting propensity of copper pipes. Campbell (1) who has studied the importance of such harmful films ie; carbon films and the glassy cuprous oxide film. These films are highly cathodic towards copper and can be formed during manufacturing process.

In the work carried out by Cruse et al (33) demonstrate that the initiation of pitting appears to be associated with the interior surface conditions of the copper pipes due to the produced films on the pipe wall.

The surface condition of copper tube as manufactured appears to have no influence on the incidence of type 2 pitting which is a hot water phenomenon but surface condition is especially of vital importance in type 1 pitting which is related to cold water (34).

In Great Britain copper tube is supplied either fully annealed, in coils for laying under ground or in straight lengths which are rigid but sufficient soft for easy binding.

Copper water pipes are used in the fully soft, half hard or hard drawn conditions. There is some evidence from the literature that annealing condition can affect the corrosion of copper. Additionally, phosphorus di-oxidised copper appears to be slightly more resistant than tough pitch copper. In the same way hard drawn tubes are more resistant than half hard tubes.

CHAPTER III

EXPERIMENTAL PHILOSOPHY / PROCEDURE

3.1.1. SPECIMEN PREPARATION:

The specimens for these experiments were prepared from copper tubes obtained from various sources. Some of the tests were carried out on samples taken from a length of copper tube removed from a hotel and suffering from pitting corrosion. The other tests used tubes obtained from plumbers merchent (BS 2871). In all cases a small part was cut from each tube and split into two halves. These halves were then flattened into a plate and copper specimens having an area of 10mm x 10mm were then cut from the plate. This gives an area of $1cm^2$ which was suitable for the semi logrithmic plots where log current density in micro-amperes per square centimetere was plotted. The soft solder and hot plate were used to attach a piece of wire to back (unexposed) faces copper pieces. These pieces with wire were then put in a mould and resin poured into the mould except exposed surface area of the specimen and left for over night to set in the resin.

The specimens were then removed from the mould and polished by a hand grinder to a 600 grit finish. All those specimens which were subjected to polarisation were passed through this process while those specimens which were used for weightloss and microscopic examination were cut straightaway from the plate in different sizes. All the unmounted specimens were also polished by a hand grinder to a 600 grit finish.

In some unmounted specimens a small hole was drilled to attach a piece of fishing thread line for the purpose of hanging in buckets and tanks.

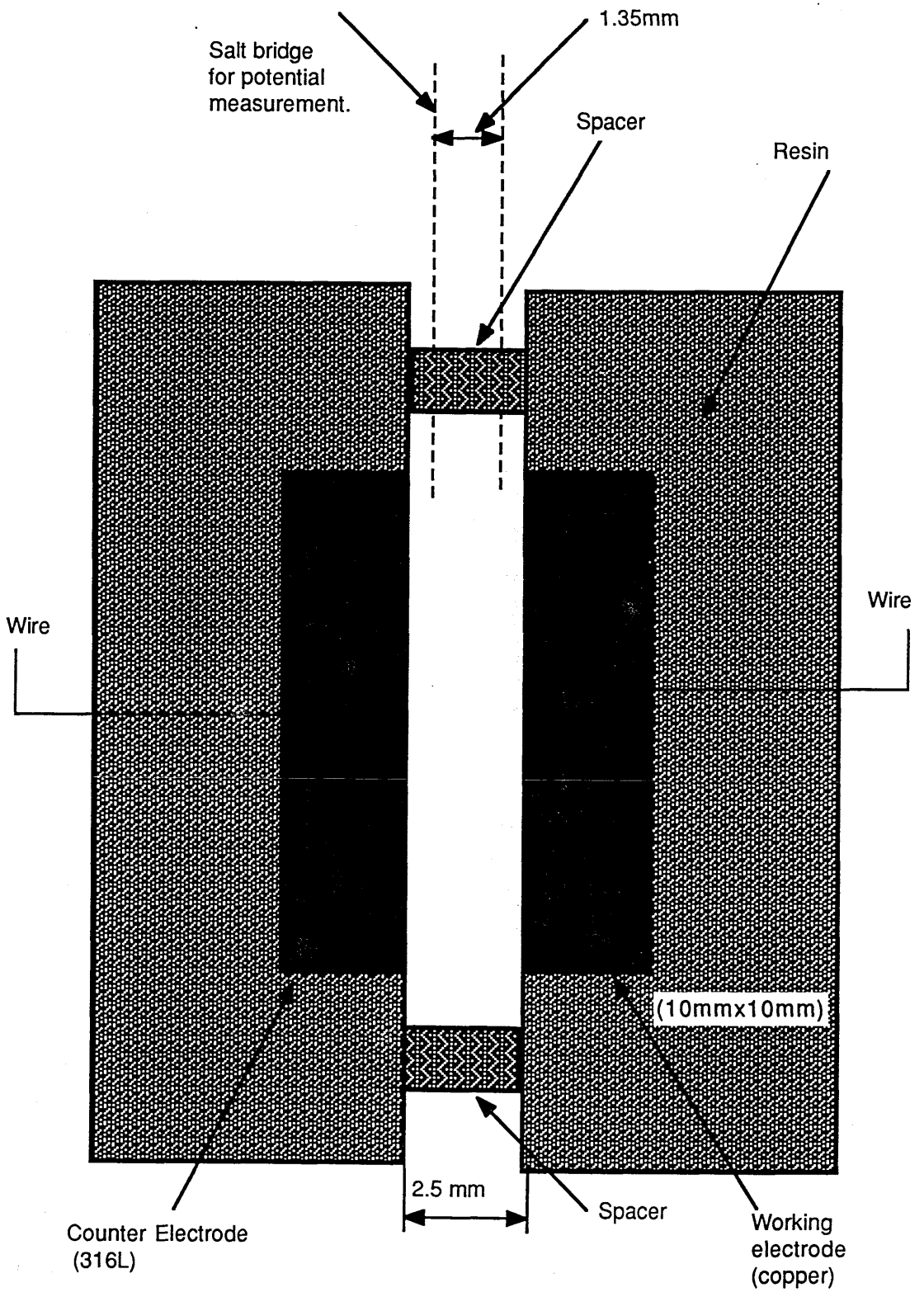
The main problem of using tapwater is that it has limited conduction properties. This factor was of major importance specially for all those specimens subjected to polarisation as to avoid complication in the experiments due to I. R drops.

There was still a need of such a compact system to eleminate the danger of I.R drops in the experiments.

A system was designed which is called a compact cell system as shown in figure 3.1. The compact cell system was designed in such a manner to place the working electrode, counter electrode and reference electrode at a minimum distance apart from each other and also to achieve identical geometrical positioning in all the polarisation experiments. The counter electrode was used 316L instead of platinium in the compact cell system. The reason for this counter electrode was to attach small spacers of 3.26 mm thickness to the electrode to achieve the task of minimum distance. The second advantage of attaching the spacres to the counter electrode was to grind the working electrode again and again and to re-use. The spacers were glued to the counter electrode and the working electrode were placed against it and held togather with plastic bands around it.

There was still one diffculty at this stage to allow reference electrode to be placed in the small gap between working and counter elecrode.

Figure 3.1 **COMPACT CELL SYSTEM**



However this was solved by the introduction of a salt bridge probe made from a mixture of potassium chloride and agar in 100 ml of distilled water. The mixture contains 30 gram of KCl plus 3 gram of agar to be dissolved in 100 ml of distilled water and heat upto $100^{o}C$ to melt the agar. Salt bridge was used as an extension to Calomel reference electrode. A tube of 1.36mm diameter was attached at the end of the salt bridge probe which makes the probe enable to be inserted in the small gap between the counter and working electrode.

In order to check the salt bridge probe, it was necessary to connect two calomel electrodes to the voltmeter and watch the reading on the voltmeter. Then one of the electrode was taken out from the beaker and put in the salt bridge probe but also keep the bottom end of the tube attach to salt bridge probe in the beaker from which one calomel electrode was taken out and now watch the reading on the voltmeter.

If the reading on the voltmeter is the same or there is only a difference of 2mV to 4mV, then the salt bridge is working properly.

If this is not the case and the difference is more , then the salt bridge is not working properly. The making of salt bridge probe is a very time consuming process, but it has a very important role in the compact cell system.

3.2.1. PROCEDURE

An aqueous corrosion is an electrochemical process and hence is suitable for studying using electrochemical techniques.

These methods have the advantage of providing rapid information on the state of a corroding component (such as instantanious corrosion rate) and also yielding useful mechanistic information.

Consequently electrochemical polarisation techniques are being used extensively in this work but are backed up by examination (including microscopical) of samples left naturally to corrode without electrochemical testing in the test environments.

Much of the investigation involves experiments which are undertaken for several months in order to obtain reasonably sensible effects of exposure time on the corrosion behaviour and, in this respect it should be noted that practical failures of copper pipes can occur in a matter of months.

In accordance with this conception experiments were performed for the corrosion of copper in different ways as given below.

1: BEAKER EXPERIMENTS.

2: BUCKET EXPERIMENTS IN LIGHT CONDITION (COLD AND HOT WATER).

3: BUCKET EXPERIMENTS IN DARK CONDITION (COLD WATER ON LY).

4: FLOWING RIG EXPERIMENT (NORMAL HOT TAP WATER ONLY).

In addition two pH tests were also carried out on the tapwater to investigate its pH stability with respect to time.

In all the experiments the compact cell system was first connected to a potentiostat (MINISTAT 251E) with aqueous environment to complete the circuit between the cathodic and anodic sites as shown in figure 3.2. Before the connection of compact cell system to potentiostat another simple system was connected to it to make sure that the potentiostat is working properly.

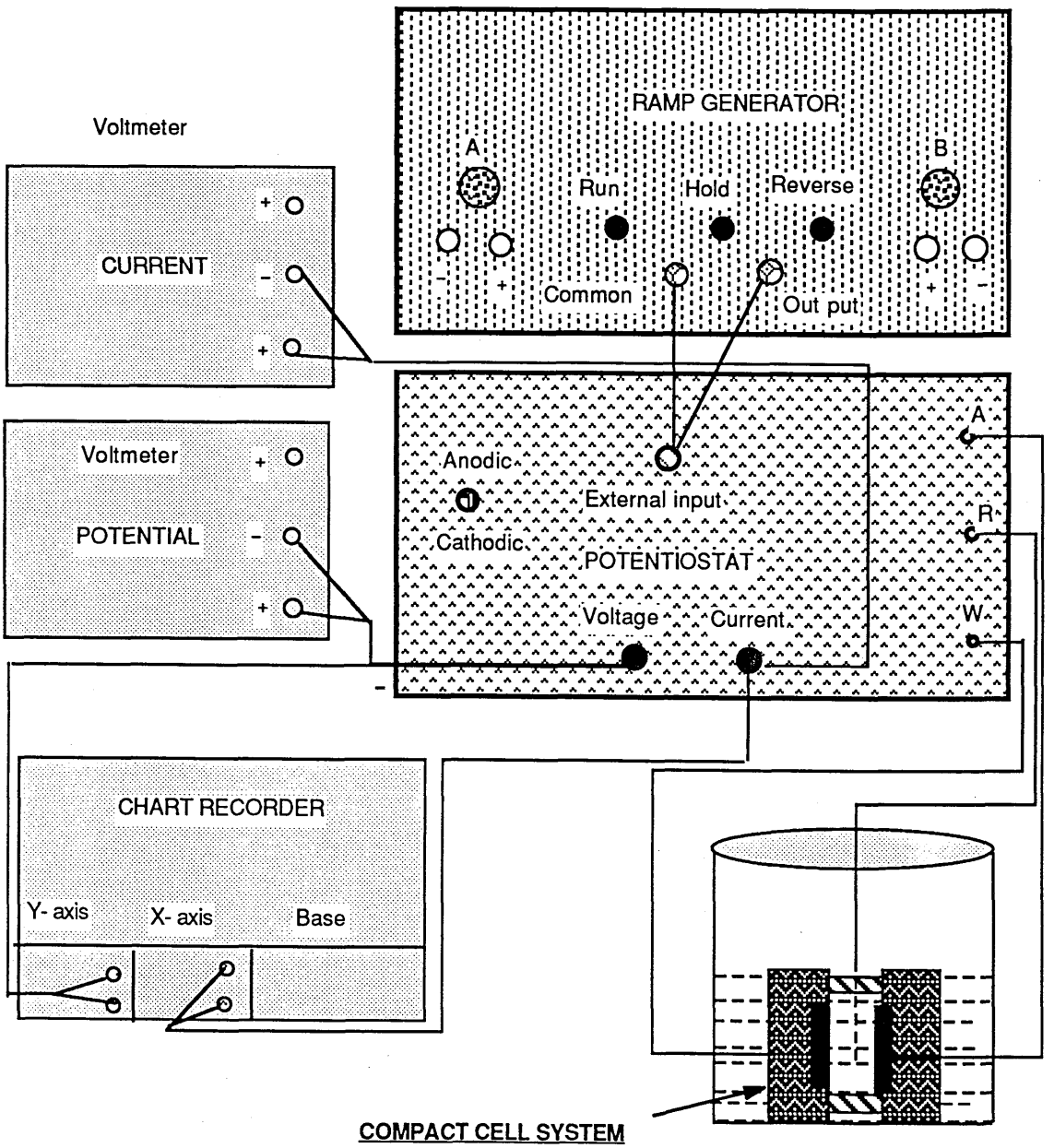
The simple system consisted of 316L as working electrode with platinium counter electrode and a calomel reference electrode in a beaker full of sea water.

When this system was connected to the potentiostat and the free corrosion potential reading on the voltmeter was satisfactory ie; with negative sign and lies in the range which is expected for 316L in sea water. Then the compact cell system was connected to the potentiostat after this operation to confirm about the function of potentiostat. A scan generator (DRG 16) was also connected to the potentiostat in order to control the increase or decrease in potential by this device instead of controlling manually during anodic or cathodic polarisation scans. In addition two voltmeter were also connected to this experimental arrangement in order to watch the specimen current and potential.

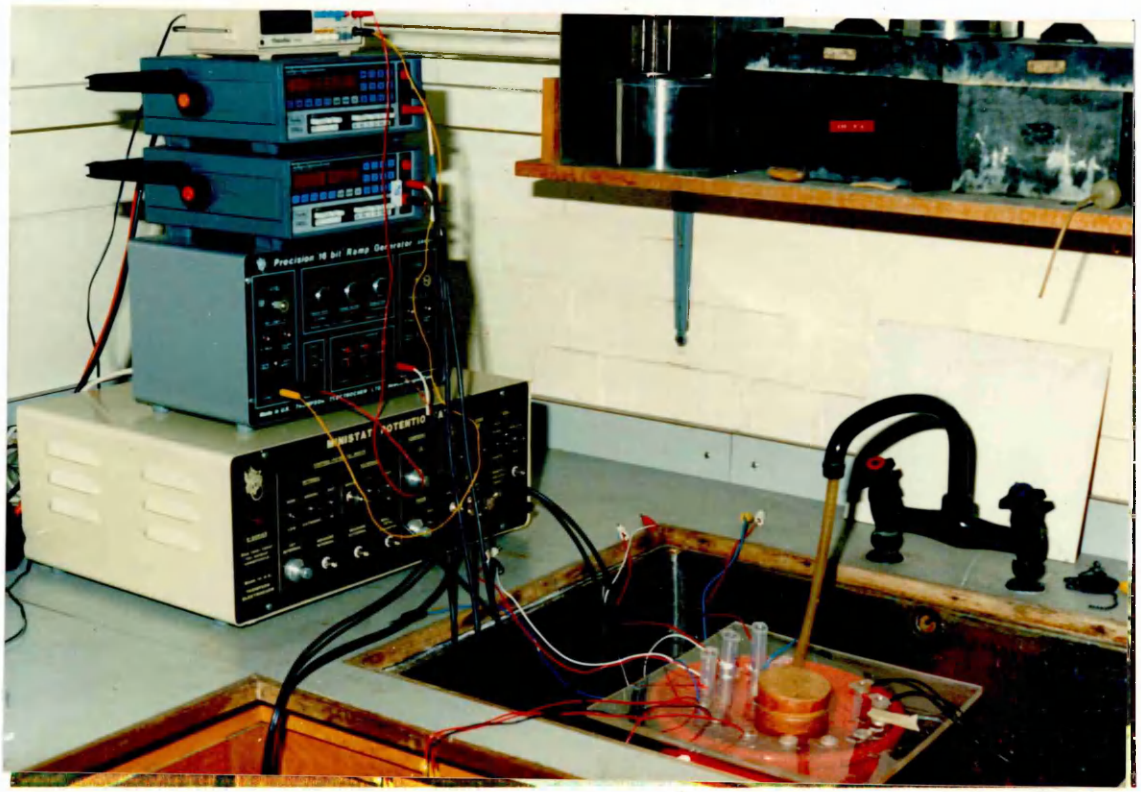
When the potentiostat was on " isolate" position, the current reading on the voltmeter-1 was zero while the voltmeter-2 reads the free corrosion potential of the specimen. The x-y plotter was also connected to the potentiostat.

Figure 3.2 **PROCEDURE FOR SCANNING**

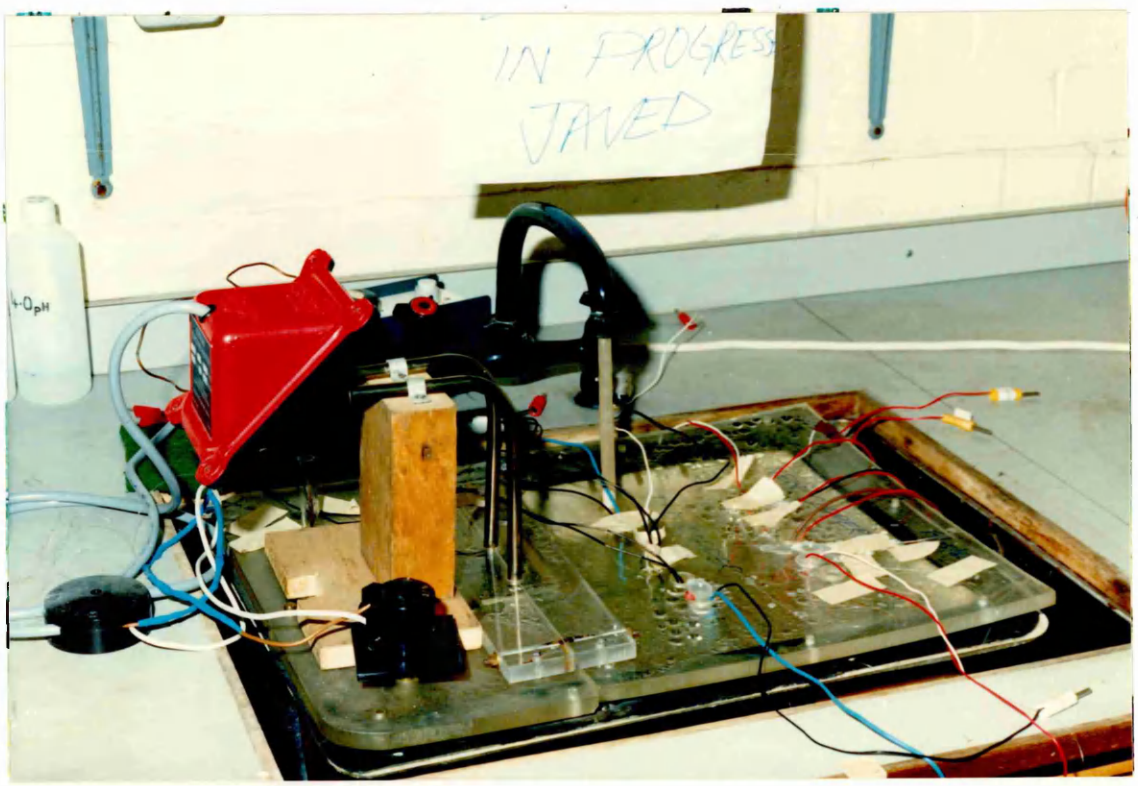
W = Working electrode R = Reference electrode A = Auxiliary electrode



COMPACT CELL SYSTEM



Photograph1 shows the experimental arrangement for copper specimens in normal hot water



Photograph 2 shows the hot water tank arrangement for copper specimens in hot water (60)

The corrosion was checked by the determination of the polarisation curves.

The polarisation experiment involves shifting the component electrode potential away from its (natural) free corrosion potential value and reading the current response.

The potential is progressively increased (more +ve) above free corrosion potential, which is called anodic polarisation. In anodic polarisation the anodic reaction is occuring on the surface of the specimen while the cathodic reaction is occuring on the counter electrode .

Similarly if the potential is progressively decreased (more-ve) below free corrosion potential, this is called cathodic polarisation.

In the cathodic polarisation the cathodic reaction is taking place on the surface of the specimen (working electrode) while the anodic reaction is occuring on the counter electrode.

In this way either the nature of anodic reaction or cathodic reaction on the surface of the specimen can be studied in detail.

The main difference between the different experiments as mentioned before was due to the condition of tapwater.

In beakers the experiments were performed in stagnant condition in both cold and hot water for copper specimens made only from the tube collected from the hotel which had been suffering from pitting corrosion [However, samples for test were taken well away from any previous attack].

In buckets the experiments were carried out in the moving cold and normal hot tap water and also in hot water at $60^{o}C$ for both grades of copper specimens.

The main aim of moving water from the bucket is to refresh the water in the bucket.

The difference between the light and dark tests was only due to the top cap of the bucket which was only performed in cold water. In the light test the top cap of the bucket was made of a transparent glass while in the dark test the top cap was replaced by a wooden cap. The small difference in the cap was only carried out to see the light affect on the developed film on copper specimens. In the flowing rig samples of new copper tubes obtained from the plumber merchant of different grades were tested only in flowing normal hot tapwater.

In this work emphasis has be placed on the study of the anodic process via " ANODIC POLARISATION". The main aim here is

a: To see if in particular experiment conditions the copper is passivated by a film or not.

b: If passive conditions prevail, to obtain an estimate of the ability of protective film to resist local break down by pitting.

This involves noting the potential , called the " PITTING POTENTIAL" at which significant current is recorded in (positive direction) anodic polarisation scan.

3.3.1. COPPER IN PLUMBING SYSTEM

Copper tube is widely used in water supply system throughout the world due to its advantages over other metals in corrosion resistance, toughness, ductility and ease of joining and fabrication. There is a large body information available dealing factors on tube construction and use which may affect the corrosion rate.

Copper tubes used in the building industry for domestic water services should be manufactured to BS 2871 (7).

This specification covers a range of sizes with appropriate tempers and wall thickness to meet a wide range of services requirements and conditions.

The part 1 of BS 2871 covers the specification of tubes designated for water, gas and sanitation purposes.

This part of British standared specifies the requirements for copper tubes in the three different conditions mentioned below.

1: Table X (B3) : Which is half hard, light gauge copper tubes supplied in straight lengths. It is suitable to made its connection by means of compression and capillary fittings. The silver brazing or suitable method of welding can also be used.

2: Table Y (B4) : Which is half hard copper tubes in straight lengths and anealed copper tubes in coils for burying under ground.

It is also good to make its connection by means of compression or capillary fittings. Silver brazing or bronz or autogenious welding can be used.

3: Table Z : which is hard drawn, thin wall copper tubes supplied in straight lengths.

Its connection can also be made by means of capillary fittings or non-manipulative type compression fittings [BS 864,part 2]. These tubes are not recomended for bendings .

The main difference between these three classifications apart from the working condition is the wall thickness of the tube.

For instance, for a 10mm nominal diameter tube,table X has a tube thickness of 0.6mm while this value for table Y and Z will be 0.8mm and 0.5mm respectively. As it is apparent from the above dimensions that if there is a condition of general corrosion within the tube, table Y would tend to give a longer life due to its thickness. This would not be the case where the problem is known to be pitting.

The basic copper used in the manufacture of all these three types of tube is phosphorous deoxidised, arsenical or non-arsenical copper to BS 1174 and BS 1172.

There was an out break of pitting corrosion failures of copper tubes carrying cold water due to the presence of carbon film which had been formed on the surface of tubes during manufacturing process.

Now it is the requirement of BS 2871 part1 that the tubes shall be free from such deleterious carbon film in the bore.

CHAPTER IV

RESULTS AND DISCUSSION

4.1.1. COLD WATER TESTS

The purpose of the experimental work described below was to look at the performance of two grades of copper specimens (B1&B3) in moving cold water. These experiments were performed in two different conditions i.e. stagnant and moving cold water condition. In the preliminary stages of this research the experiments were performed in the beakers in stagnant cold water, a number of repeated experiments were carried out over a period of time (10 days) but in every case involving a freshly abraded specimen immediately upon immersion in the water. In the later stages most of the tests were carried out in slowly moving cold water. In the slowly moving cold water (19.2 L/hr,21.6 L/hr,25.2 L/hr) the experiments were performed in different buckets. A number of flat copper specimens were immersed in the slowly moving cold water buckets at the same time. In the slowly moving cold water the experiments were performed in two different conditions ie light and dark condition. The aim behind these different conditions was to study the effect of illumination on the developed protective film on the surface of both grades of copper specimens. The two buckets (21.6 L/hr,25.2 L/hr) were placed in two seperate small rooms having no windows inside the laboratory. These buckets were exposed to room light (fluorescent tube light).

The specimens in the bucket which was covered by a transparent glass cap were considered under light condition.

The specimens in the bucket which was covered by a wooden cap were considered under dark condition. A number of holes were drilled in the top cap of the buckets for saltbridges (an extension to reference electrode) which were also used for the leads of the specimens.

In the dark condition insulation tape was also used to ensure that the holes were fully covered and the specimens inside the bucket were in dark. Also in slowly moving cold water (21.6 L/hr,25.2L/hr) some specimens were used to measure their free corrosion potential as a function of time and the others were subjected to polarisation scans over a period of time.

In this work, it has been assumed that the potential at which the measured current starts to increase relatively rapidly (compared to prior potentials) represents the onset of protective film breakdown.

The results given in figure 1 shows the performance of old copper specimens (B1) in stagnant condition in the preliminary stages in the beaker tests. The results indicate the current response with potential from the beginning of the specimens in the stagnant condition.

The results given in figure 2 and 3 demonstrates the behaviour of old copper specimens (B1) in slowly moving cold water (19.2 L/hr). In the slowly moving cold water the more negative free corrosion potential for some specimens were observed after a few days of immersion.

The anodic polarisation results obtained at different exposure time in slowly moving cold water [figure 2&3] indicate that a very low current (meaning in terms of protective film) was observed with the rise in potential in the beginning as compared to the specimens in stagnant condition [figure1] upon immediate exposure.

The difference in the two sets of experiment was that immediately after exposure time the potential in the stagnant water was more noble as compared to the potentials in moving cold water after a day or few days of immersion.

This may be because in the beaker the water absorbs some contents from the atmosphere (for instance CO_2 from the air) which drop the pH of the water. Such a decrease in pH would also be expected to stimulate the corrosion rate of copper.

The action of carbon dioxide with water produce carbonic acid and increase the hydrogen ion concentration. Since copper is more noble than hydrogen and the metal is not easily attacked by acids in the absence of dissolved Oxygen. In the presence of dissolved oxygen, copper corrosion is accelerated by increased hydrogen ion concentration which results due to carbon dioxide (35). The anodic polarisation results obtained at different exposure time in moving cold water indicate the formation of a protective film on the surface of the specimens [figure 2&3] because in the moving cold water the pH does not drop to such a lower value as was in stagnant water. The pH in moving cold water were in the range of 8.13-8.59 while this range was 6.8-7.5 in the stagnant condition.

The results given in figure 4 demonstrates the trend in free corrosion potential for both grades of copper specimens with response to time in slowly moving cold water (21.6 L/hr). The results indicate that the free corrosion potential of both specimens were shifted in the noble direction in the first period of about five days for old copper and for about 12 days in case of new copper.

Then a slow drop in potential was observed for both specimens which was recovered on the next day in case of old copper specimen but was continued in the next three days for new copper specimen.

The fluctuations (slow drops) in free corrosion potential were observed for both specimens with the length of time may indicate some local rupture in the developed protective film on the surface of the specimens. Apart from these slow drops in potential a significant drop in potential was observed for old copper specimen after 15 days of immersion.

This significant drop in potential of old copper may indicate the presence of cuprous chloride in the existing protective film on the surface of the specimen which will be discussed later in this section in the light of previous investigations by other investigators in this field (17,36,37).

They have suggested that such big drop in potential may occur due to the presence of cuprous chloride in the surface layer.

The results also indicate subsequent gradual increase in potential of both grades of copper specimens with the length of immersion time as apparent from the free corrosion potential verses time curve (figure 4).

The results given in figure 5 demonstrates the performance of both grades (B1&B3) of copper in a different set of experiment in moving cold water (21.6L/hr). It is worthwhile to mention that more negative free corrosion potentials were observed for new copper specimens (B3) as compared to old copper (B1).

The same change has also been noticed in the comparison work of Glasgow water versus Lancashire water for both grades of copper. As it has been discussed in the comparison work that perhaps this property of new copper may be related to its metallurgical surface condition of the material.

The results indicate that the breakdown of the protective film occurs at about -90mV for new copper specimen while this value was about +50mV for old copper specimen. The passive current was in the range of about1-2μA for old copper specimen and about 4μA-5μA for new copper specimen.

The increase in current above breakdown potential was high for old copper specimen as compared to new copper specimen.

The above results of old copper specimen after one day of immersion have been compared with the results of old copper specimen 1 after one day of immersion in figure 2. Both the passive current range (about 1-2μA) and the breakdown potential was the same for both specimens. The increase in current above breakdown potential was high for both specimens. The other difference was that both specimens were exposed in different buckets with a different flow rate ie 19.2 L/hr and 21.6 L/hr respectively.

The results given in figure 6 shows the **cathodic** behaviour after one day of exposure for both grades of copper in moving cold water.

These specimens were not subjected to any prior polarisation scan. The same behaviour of more negative Ecorr was observed for new copper specimen as compared to old copper. The cathodic polarisation scans obtained for both grades of copper specimens indicate that the increase in current with response to potential was high for new copper as compared to old copper. However, in both cases, the currents recorded for quite high **cathodic** overpotential were only a few microamperes.

The results given in figure 7 demonstrates the behaviour of both grades of copper after six days of immersion in moving cold water and these specimens had not been subjected to any polarisation tests prior to six days.

The results indicate that both grades of copper specimens were trying to develop a protective film with the length of time because low current with response to potential was observed in the beginning for these two specimens as compared to the specimens given in figure 5. The breakdown of protective film occurs at about -70mV above Ecorr for new copper specimen and this value was about 20mV above Ecorr for old copper specimen. The passive current was in the range of about 1-2μA for old copper specimen and about 3-4 μA for new copper specimen. The increase in current above breakdown potential was higher for old copper specimen as compared to new copper specimen.

The results of old copper specimen in this figure have been compared with the results of old copper specimen 6 in figure 2. The decrease in passive current and breakdown potential were observed for this old copper specimen (figure 7) as compared to the old copper specimen in figure 2.

The results given in figure 8 shows the **cathodic** performance of both grades of copper specimens after six days of immersion in moving cold water without prior polarisation. This time again very low current was recorded for quite high cathodic overpotential and the time has not changed the curves. The second difference was the more negative Ecorr for these specimens after six days of immersion [figure 8] as compared to figure 7.

Some specimens were exposed in the cold water (21.6 L/hr) tests for extended periods before any polarisation scans were carried out.

The results given in figure 9 shows the performance of both grades of copper specimens in moving cold water after 105 days of immersion. The results indicate that the performance of old copper was slightly better than the performance of new copper.

The breakdown of protective film occurs at about +100mV and about+90mV respectively. The increase in current above breakdown potential was high for new copper specimen as compared to old copper specimen.

The above results of old copper specimens have been compared with the results of specimen 9 in figure 2. The breakdown potential value of specimen 9 in figure 2 was about +80mV with the passive current range of less than 1μA after 9 days of immersion. The breakdown potential of the above old copper [fig:9] specimen was +100mv with a passive current range of about 1μA-2μA after 105 days of immersion.

The results given in figure 10-12 shows the performance of both grades of copper in moving cold water after one year of immersion without any prior polarisation.

These results are interesting and the important point is that both grades of copper behaves very similarly.

The Ecorr of old copper specimen was negative by a few millivolts (10mV) than the Ecorr of the new copper specimen. The breakdown of protective film occurs at about +80mv for new copper specimen as well as for old copper specimen. The passive current was in the range of about 2μA-3μA for new copper specimen while this range was about 3-4 μA of old copper specimen.

The increase in current with response to potential was behaving in the same manner for both grades of copper specimens.

The above results have been compared with the results in figure 9. The breakdown potential of both grades of copper was not much different in the two sets of experiments with different immersion time. The results also indicate the increase in the passive current range for the old specimens with response to immersion time while the passive current range was the same for the new copper specimens.

In the anodic polarisation scan which was carried out after the cathodic scan the breakdown of protective film occurs at about +60mV for new copper specimen and the passive current was in the range of about 2μA-3μA as given in figure 11.

In the **cathodic** polarisation scan the very low current was observed for quite high cathodic overpotential. The anodic polarisation scan was performed after the cathodic polarisation scan.

In the anodic polarisation scan performed after the cathodic scan the breakdown of protective film occurs at about +50mV for the old copper specimen and the passive current was in the range of about 1μA-2μA as given in figure 12.

Similar behaviour for the old copper specimen was observed in the **cathodic** polarisation scan as was observed for new copper. The increase in current above breakdown potential was rather high for new copper specimen as compared to old copper specimen (figure 11-12).

The results given in figure 13 and 14 are re-plots of the results from the previous graphs to demonstrates the overall performance of both grades of copper with the length of immersion time in moving cold water.

The above results suggests a drift in the positive direction of free corrosion potential with the length of time for both grades of copper.

This may well be a factor in the corrosion of copper in this water. It is evident from the literature (24,35) that regardless of the types of pitting, the avoidance of more noble potential is regarded as the best preventive method against copper pitting.

The noble free corrosion potential behaviour of copper specimens immersed in this water has also been observed in the comparison of Glasgow water versus Lancashire water which will be discussed later.

The interesting feature of these results was that slightly negative free corrosion potential were observed for the specimens after approximately one year of immersion as compared to the free corrosion potential of the specimens after 105 days of immersion.

This slow drop in Ecorrs of the specimens may be related to some changes taking place in the properties of the protective film developed on the surface of the specimens with length of time.

Also the results indicate a good correlation in the breakdown potential and passive current values for two different grades of copper after one year of immersion.

This may indicates a kind of similarity in the properties of the developed protective film on the surface of the specimens.

4.1.2. DARK CONDITION

The main difference between light and dark conditions was the top cap of the buckets as mentioned earlier. The specimens in the bucket which was covered by a transparent glass cap were considered under light condition While the specimens in the bucket which was covered by a wooden cap were considered under dark condition. The aim behined these two different conditions was to study the effect of light on the developed protective film on the copper specimens.

The results given in figure 15-16 demonstrates the trend in free corrosion potential for both grades of copper specimens with response to time in slowly moving cold water (25.2 L/hr) under the above mentioned dark condition. Four copper specimens (two of each grade) were immersed in moving cold water and their corrosion potential were recorded as a function of time for about 105 days.

The free corrosion potential of the specimens shown in figure 15 were first recorded from the first day of immersion while the free corrosion potential of the specimens shown in figure 16 were recorded after 12 days of immersion.

The results in both figures indicate some slow drops in potential for all specimens with the length of time at irregular intervals which indicare that local rupture may have developed in the protective film on the surface of the specimens. The results also indicate that these slow drops in potential has been followed by a positive drift in potential with the length of time.

These results also provide a good base for those results shown in figure 4 under light condition because no significant drop in potential was observed for old copper specimen under dark condition as was observed for old copper specimen under light condition.

The results given in figure 17-18a shows the performance of both grades of copper specimens under said different conditions i.e. dark and light. Four copper specimens (two of each grade) were immersed in moving cold water (25.2 L/hr) under dark conditions.

The specimens were left in the dark condition for two weeks and then two of them were transfered (one of each grade) to cold water (21.6 L/hr) under light condition. The free corrosion potential of these specimens were measured as a function of time in the two conditions for about three months.

The results given in figure 17-17a indicate the performance of new copper specimens in the two different conditions.

The new copper specimens demonstrated similar performance under dark condition as were observed for the new copper specimens in figure 15-16 because again small potential drops at irregular intervals and a positive drift in potential was observed for this specimen.

In the light condition a slow potential drop was observed for new copper specimen after about one month of immersion and was continued for about six days.

The similarty between the two drops in potential of two different grades of copper was that the drop in new copper was also recovered in the six days while the considerable drop which was observed in the potential of old copper specimen (figure 4) for one day and the drop was also recovered on the next day.

The results in figure 18-18a shows the performance of old copper specimens under dark and light condition. The specimens were first immersed in the dark condition and then one of them was transfered to light condition (21.6 L/hr) after two weeks of immersion in dark.

The results indicate that the behaviour of the old copper under dark condition is not much different from the behaviour of the old copper specimens in figure 15-16 because similar slow drops in potential was also observed for the old copper specimen under dark condition as was in figure 15 and 16 and followed by a potential drift in the positive direction.

The results of old copper specimen under light was behaving in different manner from the old copper specimen in figure 4.

Such significant drop in potential was not observed for this old copper specimen under light as was observed for the old copper specimen in figure 4.

This may well be related to the properties of the film developed on the surface of the specimen during the first two weeks of immersion in the dark condition. The fluctuation in potential with the length of time may be due the local rupture in the film. The anodic polarisation scan of the specimens given17-18a is given in figure 19 and 20.

The results given in figure 19 demonstrate the performance of both grades of copper specimens in moving cold water(25.2 L/hr) under dark condition with the length of time. The breakdown of protective film occurs at about +80mV for new copper specimen and for old copper specimen. The passive current range was about 2μA-4μA for both grades of copper. In comparing these results with the results given in figure 9, the results indicate approximately similar breakdown potential and passive current range for both grades of copper specimens under two different conditions. Also the Ecorr of the specimens under two different conditions is not much different from each other. The current above breakdown potential is behaving in a slightly different manner in the two conditions. The current above breakdown potential was high for new copper specimen as compared to old copper specimen in the light condition while in the dark condition the current above breakdown was high for old copper specimen rather than new copper specimen.

The results given in figure 20 demonstrate the performance of both grades of copper specimens exposed to both conditions. These specimens were first immersed in the dark condition and left there for about two weeks. These specimens were then transfered to moving cold water under light condition and were there for about 70 days.

The anodic polarisation scans of the specimens were carried out in the moving cold water under light condition. The breakdown of the protective film occurs at about +10mV for new copper specimen while this value was about +40mV for old copper specimen. The passive current range was about 1μA-2μA for new copper while the passive current range for old copper was about 2μA-3μA. The current above breakdown potential was high for new copper specimen as compared to old copper specimen.

The results obtained for both grades of copper with response to time in moving cold water shows good correlation in the breakdown potential and passive current values.

This correlation in both grades of copper may be related to the similarity in the developed corrosion product layer and indicate satisfactory performance in moving cold water for the period involved in this work. The results obtained for both grades of copper under dark condition has not been performed systematically but the work so far carried out here suggest the influence of light on the corrosion product layer. The results also demonstrate the effect of illumination on the potential of copper specimens because a considerable drop in potential was observed for old copper specimen after 16 days of immersion. This drop in potential suggest the presence of cuprous chloride (CuCl) on the surface of the specimens as observed by investigators (17,36,37).

Pourbaix (36) has suggested that the presence of cuprous chloride in the film which is responsible for such depression in potential under illumination.

Lucey (17) has discussed two types of film on the surface of copper specimens under light condition which can be conveniently recongised by their potential behaviour.

The presence of cuprous chloride (CuCL) in the film will develop a more negative potential under illumination while the presence of cuprous oxide in the film will develop a more positive potential on illumination.

The above results also suggests that these fluctuation in potential with the length of time may well be related to the local rupture and its re-formation in the film as was observed by the investigators. The above described sudden drop in potential under illumination and the drift in noble direction suggest the presence of both cuprous chloride and cuprous oxide in the protective film on the surface of the specimens.

The current above breakdown potential was high for new copper specimen under light condition while the current above breakdown was slightly high for old copper in the dark condition.

The specimens exposed to two different conditions (figure 20) suggests that light may have some effect on the developed protective film on new copper specimen because in the dark condition the performance of new copper was slightly better than the performance of old copper.

In the other way the performance of old copper was slightly better in the light condition.

There is some evidence from the literature that light have some influence on the protective film if the film contains cuprous chloride.

The above results obtained for both grades of copper under light and dark condition may also suggest the presence of both cuprous oxide and cuprous chloride because of such negative drops and positive drift in potential.

Table 1:- The table shows some of the parameters for both grades of copper in moving cold water.These parameters include Ecorr, Ebreak, Ipassive, I above E break and the time of immersion.

Moving cold water

FIGURES AND BATCH NO	TIME OF IMMERSION (DAYS)	FREE CORROSION POTENTIAL (mV)	BREAKDOWN POTENTIAL (mV)	PASSIVE CURRENT (μA)	CURRENT ABOVE BREAKDOWN (μA)
B1	ONE DAY	-83	50	1-2	High
B1 2	SIX DAYS	-60	40	2-3	Slow
B1	NINE DAYS	-78	80	Less than 1	High
B1	ONE DAY	-123	50	1-2	High
5 B3		-291	-90	4-5	Slow
B1	SIX DAYS	-95	20	1-2	High
7 B3		-255	-70	3-4	Slow
B1	105 DAYS	-12	100	1-2	Slow
9 B3		-23	90	2-3	High
B1	ONE YEAR	-41	80	3-4	Same Response
10 B3		-31	80	2-3	
B1	90 DAYS [DARK]	-18	80	3-4	High
19 B3		-30	80	2-3	Slow
B1	90 DAYS Dark & Light	-28	40	2-3	Slow
20 B3		-57	10	1-2	High

4.1.2 Visual examination

The surface of some mounted and unmounted copper specimens were examined under low power microscope. These are as follows.

Photograph 1 shows that a black/blueish layer of corrosion product was observed on the surface of both grades of copper specimens after 105 days of immersion in moving cold water.

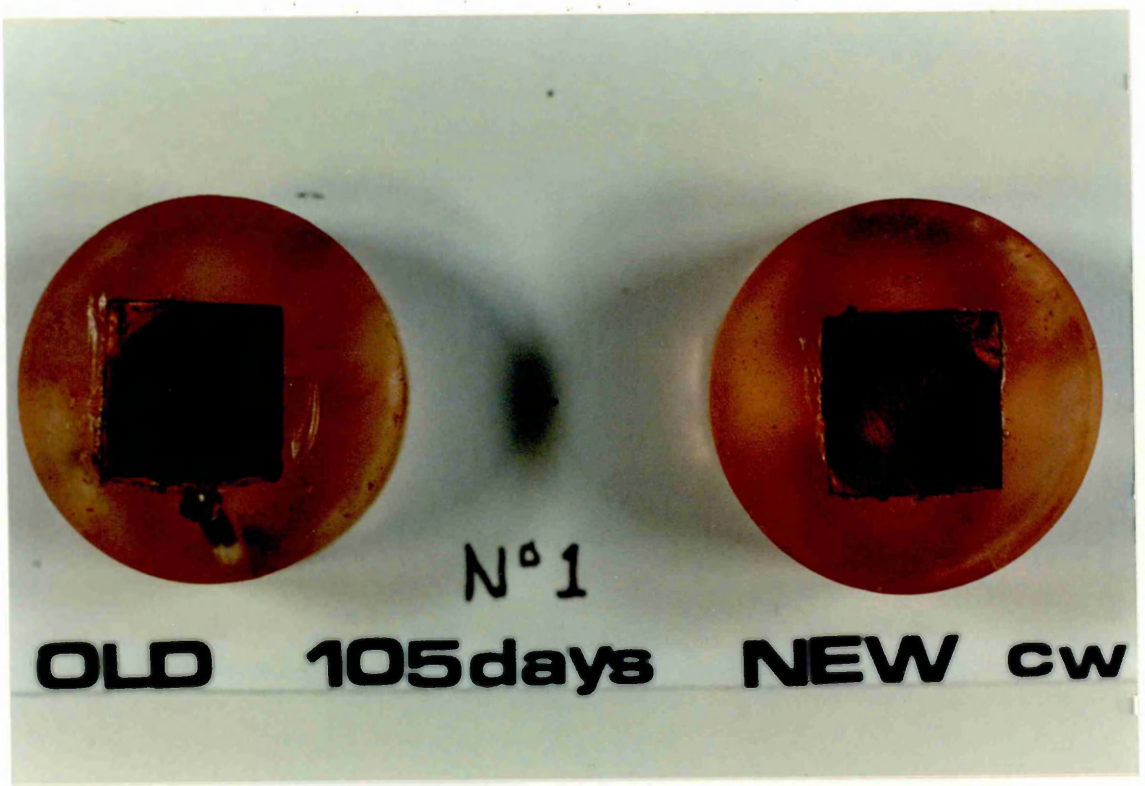
Photograph 2 shows that a black/brown layer of corrosion product on the surface of both grades of copper specimens was observed after 88 days of immersion under dark condition in moving cold water.

Photograph 2A shows that a black/brown layer was observed on the surface of copper specimens exposed to both dark and light condition. These specimens were first immersed in dark condition and left there for two weeks and then shift to light condition.

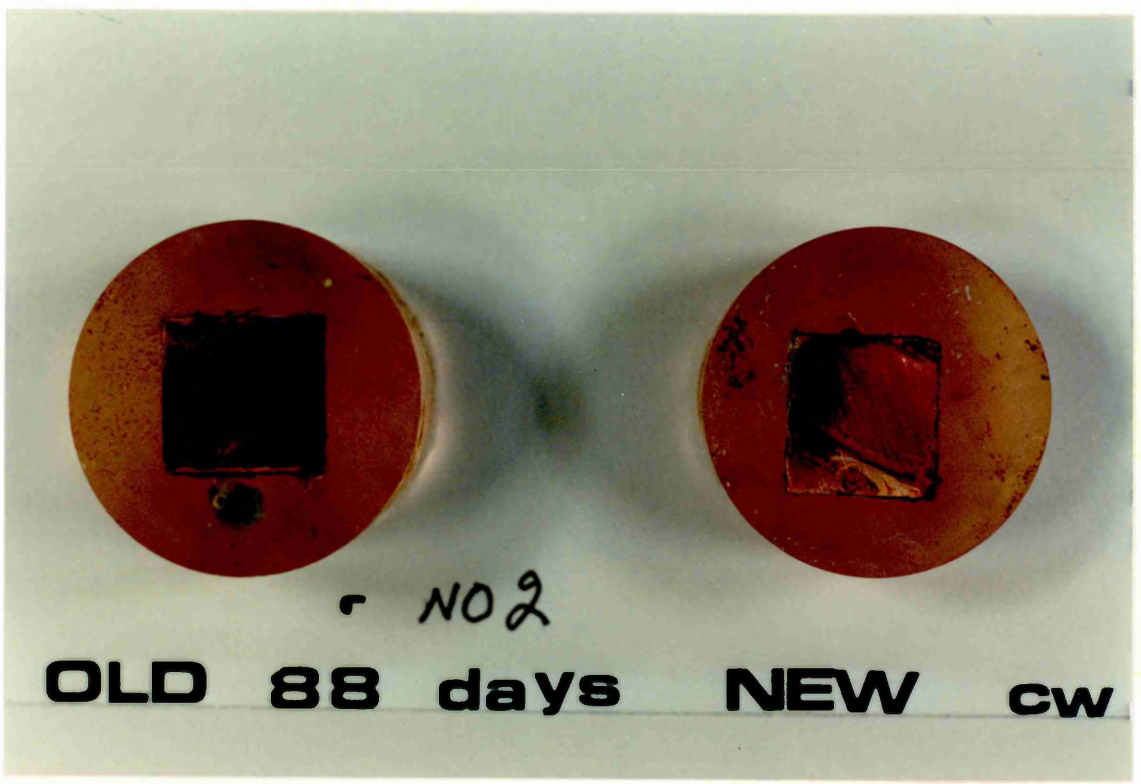
photograph 3 indicate the surface of copper specimens after one year of immersion in moving cold water. The colour of the corrosion product was green/black on old copper specimens and mostly black on new copper specimen.

Photograph 3A shows the surface of copper specimens after one year of immersion in moving cold water. These specimens were subjected to both cathodic and anodic polarisation. Similar corrosion product layer was observed on these specimens as were observed on specimens in photograph 3.

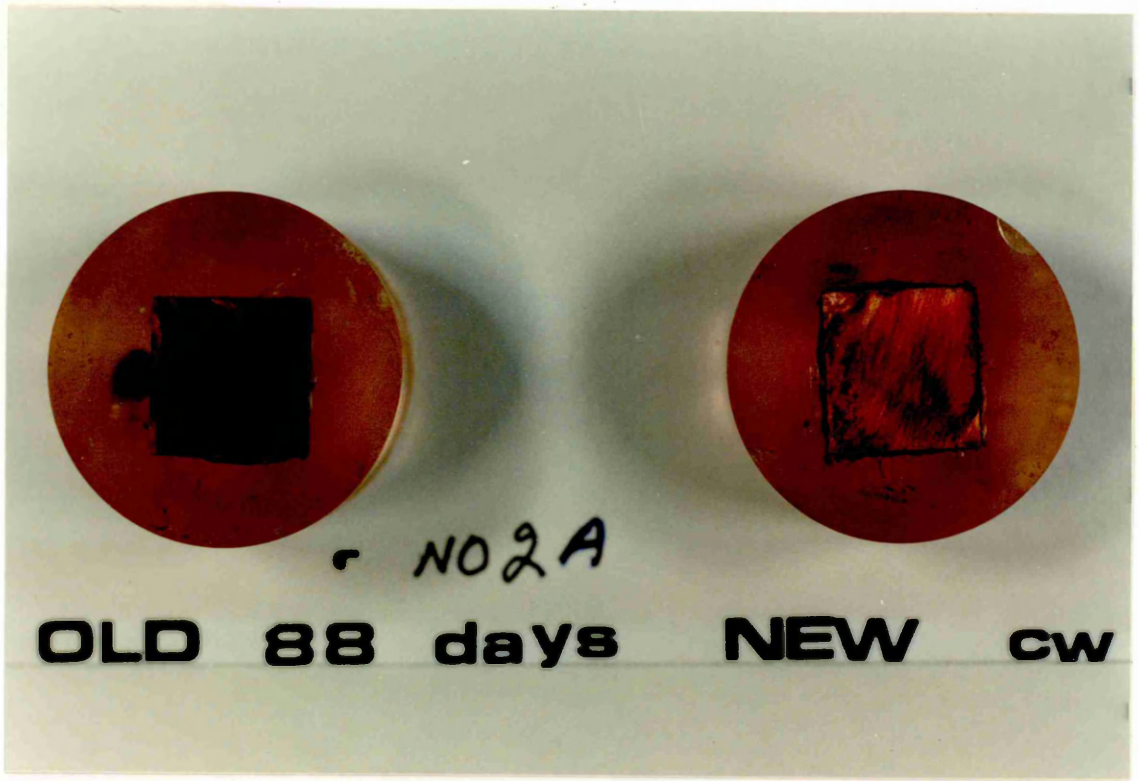
Photograph 3A* shows the surface of unmounted specimens after one of immersion in moving cold water. A fairly uniform brown/green corrosion product was observed on the surface of both copper specimens.



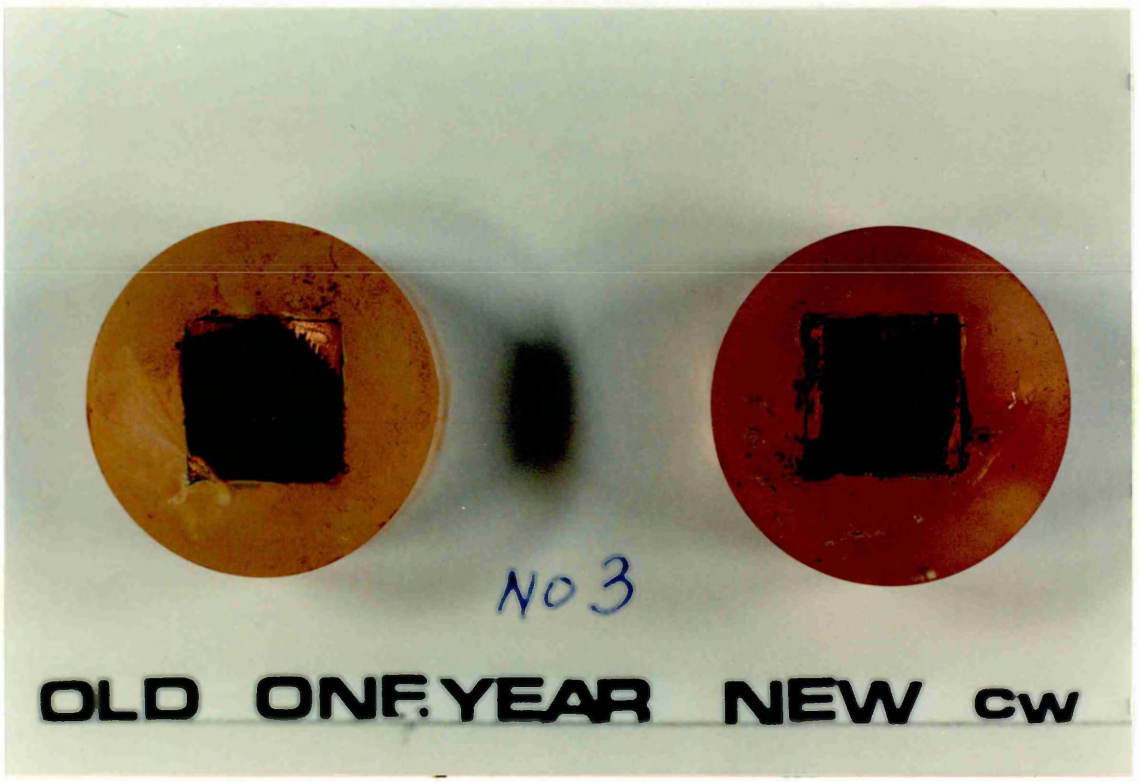
Photograph 1 shows the surface of copper specimens after 105 days of immersion in cold water.



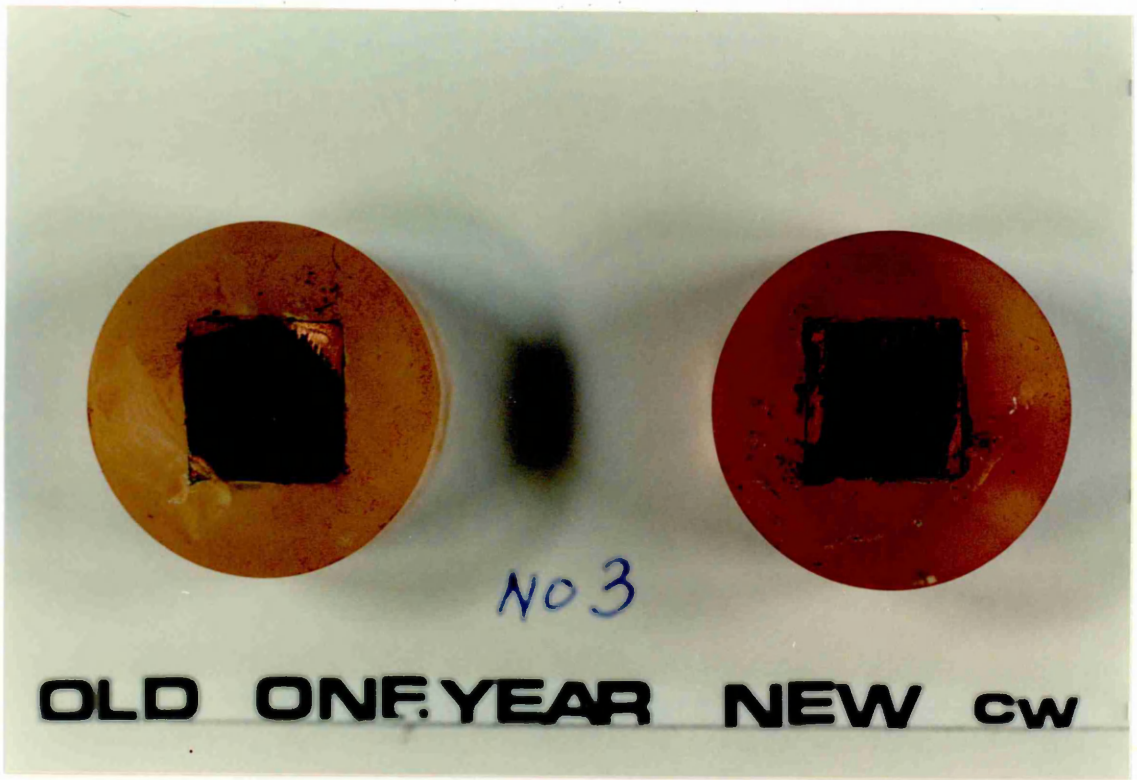
Photograph 2 shows the surface of copper specimens after 88 days of immersion in dark condition.



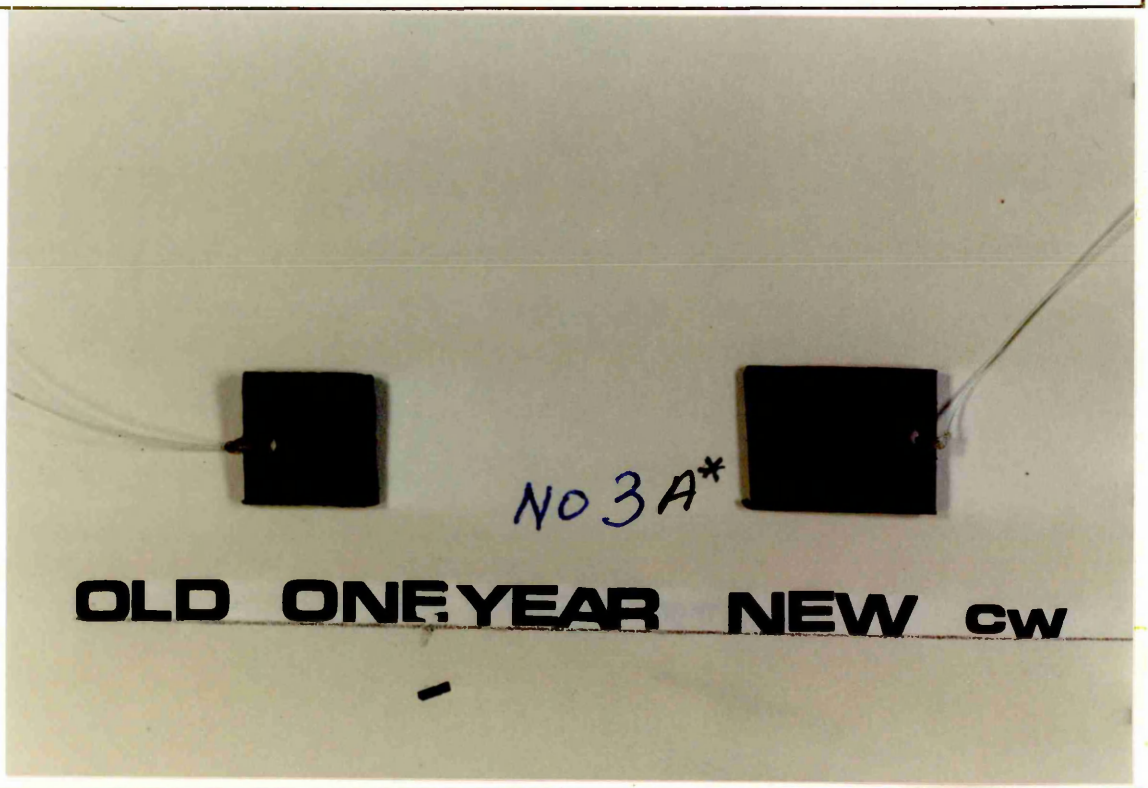
Photograph 2A shows the surface of copper specimens after 88 days in both dark and light cond.



Photograph 3 shows the surface of copper specimen after one year in cold water (Anodic scan).



Photograph 3A shows the surface of copper specimens after one year (Cathodic & Anodic) C/W.



Photograph3A* shows the surface of unmounted specimens after one year of immersion in C/W.

4.2.1. pH TESTS

The pH value is considered one of the most important guide parameter from the aspect of aggressivity and corrosivity of a water. The influence of pH on the dissolution of copper has been evident from the work of Tronstad et al as described by Sato (2). They have demonstrated that the variation of copper ion concentration with pH value is related to the solubility of copper compounds such as oxide and basic salts because in most practical cases the acidic water with low pH value are highly cuprosolvent. The effect of pH in corrosion process has been noticed by many investigators which has been extensively discussed in the literature section.In view of the above and previous discussion two pH tests were carried out in water as follows.

In one test, samples of water were taken from the laboratory for a period of five days. One sample was closed to the atmosphere in a bottle part full of water but containing some residual air and the other was in a beaker open to the atmosphere. The pH measurements were taken in this way are summarised in table 1.

In the second test samples were taken every day for thirteen days by filling a bottle to overflowing to remove any air. The samples were closed to the atmosphere and left for five days in the bottle. The pH values taken both at the time of sampling and then immediately after opening the bottle five days later as shown in table 2.

These are very interesting in that they show that , even in a system which is closed to the atmosphere (pipe), the pH falls although at a slower rate than when open to the atmosphere.

The water open to the atmosphere displayed an immediate (one day) fall in pH from about 8.5 (as in fresh water) to about 6.8 and thereafter was fairly steady.

Initially this was considered to be the well-known effect of carbon dioxide from the air which hydrolyses in water,

$$CO_2 + H_2O = H_2CO_3$$

The carbonic acid is a weak acid and therefore the pH of the water is reduced.

The water in partly filled, closed bottle also experienced a fall in pH to about 6.8 to 7.0 but a slower rate (several days).

However, the results of the samples in completely filled, closed bottles indicates that some other factors may be contributing to decrease in pH.

It is understood that the buffer capacity has great influence on the tendency of a water to affect its ability of protective coatings.

The alteration of pH In Glasgow water system has been studied by Watker (23).. She found that in Strathclyde the pH of the water is in the order of 9 as it leaves the main water treatment works. This pH value declines throughout the system upto about1.5 units. Also the reactions occurring within a main distribution system are various which effect the pH in the system. She appears unable to exactly tie down the reason for such pH decrease but she suggests that the presence of humic acid in the water distribution system may be the reason for such decline in pH because she found that humic acid does complex with Calcium,Iron and Aluminium causing the liberation of hydrogen ions into the water system.

She has also suggested that the removal of humic acid molecules prior to the distribution system may be advisable.

Further consideration of this phenomenon is required but, from a practical point of view, it provides strong indications that stagnant water in non-operational systems or dead legs of a pipe system may become more corrosive by the virtue of these decrease in pH.

Table 2:- Samples of tapwater were taken for a period of five days to see the variation in pH. One sample was closed to the atmosphere in a bottle part full of the water but contains some residual air and the other was in a beaker open to the atmosphere.

SAMPLES	Start of Experiment	Day One	Day Two	Day Three	Day Four	Day Five
Bottle	8.5	7.22	7.04	6.91	6.87	6.83
Beaker	8.5	6.85	6.79	6.79	6.83	6.97
Bottle	- - -	8.45	7.26	7.05	6.96	6.89
Beaker	- - -	8.45	6.81	6.78	6.81	6.88
Bottle	- - -	- - -	8.54	7.23	7.11	6.97
Beaker	- - -	- - -	8.54	6.81	6.85	6.83
Bottle	- - -	- - -	- - -	8.50	7.25	7.20
Beaker	- - -	- - -	- - -	8.50	6.85	6.80
Bottle	- - -	- - -	- - -	- - -	8.50	7.44
Beaker	- - -	- - -	- - -	- - -	8.50	6.87

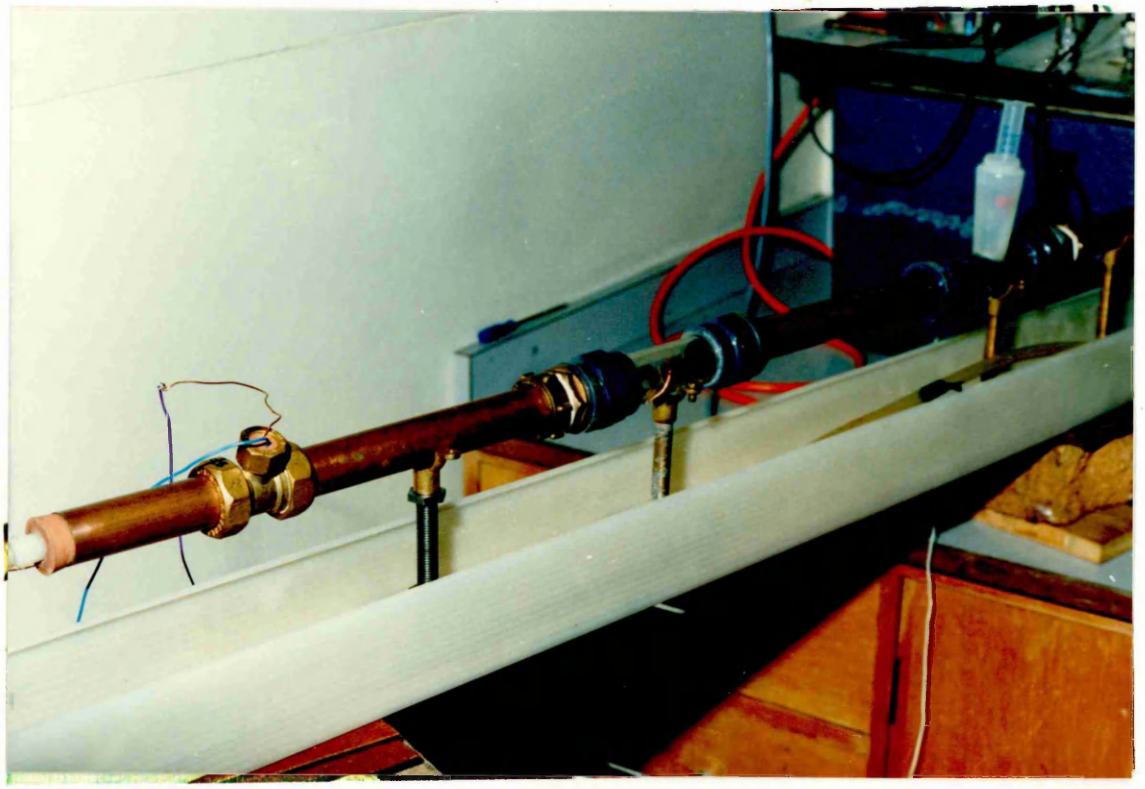
Table 3:- Samples of waterfor pH test were taken from the second floor of the corrosion laboratory. The bottle was full of water and closed to the atmosphere and left for five days. The pH was measured immediately for all samples after opening the bottle.

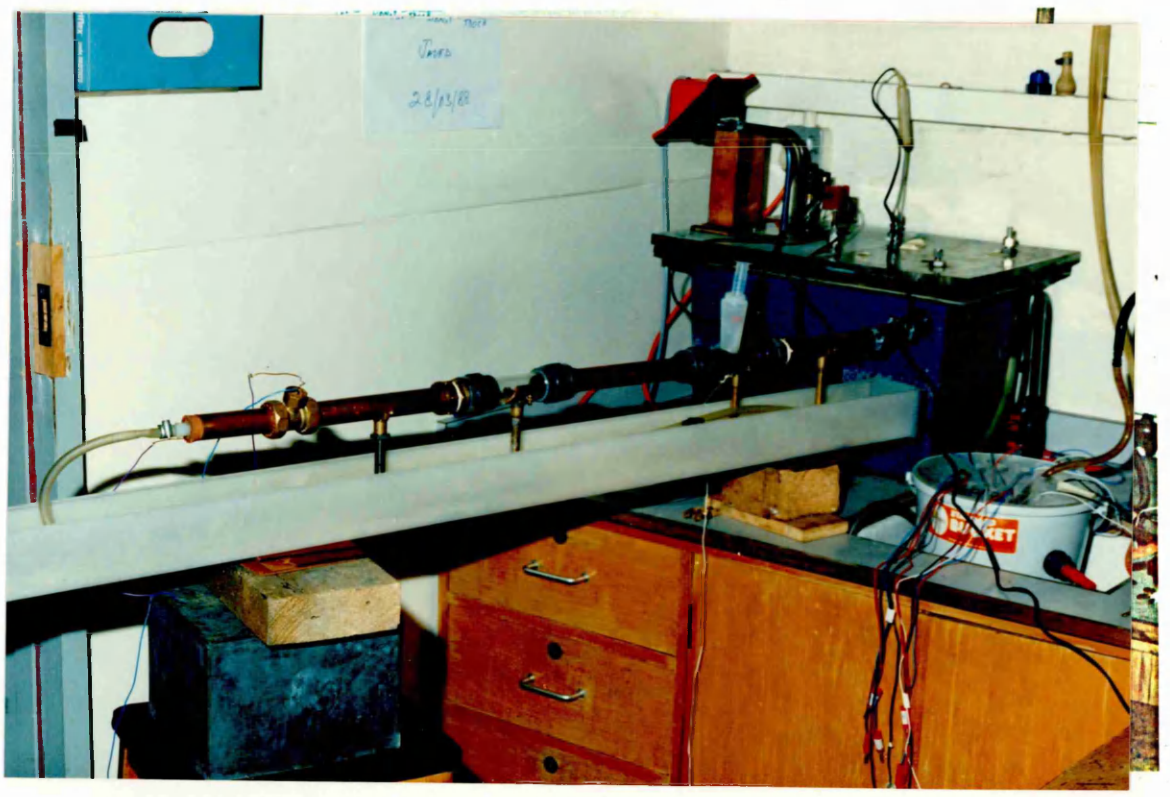
NO	SAMPLES	pH OF FRESH TAPWATER	pH AFTER FIVE DAYS
1	A	8.6	7.64
2	B	8.46	7.75
3	C	8.20	7.58
4	D	8.53	7.68
5	E	8.12	7.65
6	F	7.93	7.73
7	G	8.20	7.85
8	H	8.04	7.95
9	I	8.36	7.89
10	J	8.12	7.78
11	K	8.21	7.55
12	L	8.35	7.71
13	M	8.59	7.99

4.3.1. MOVING HOT TAP WATER

This part of the experimental work describes the performance of different grades of copper in moving hot tap water (40-50^{o}C). These experiments were carried out in two different ways i.e. moving water buckets and in a flowing rig. The flow rate of the buckets was 23.4 L/hr and 39.6 L/hr respectively. These buckets were also designed in the same way as was designed for moving cold water. In the same manner holes were drilled in the top cap of the buckets for saltbridges which were also used for the leads of the specimens. These buckets were placed in a small room under fluorescent room light only and no test has been performed for the copper specimens in moving hot tap water under dark condition. In the bucket with a flow rate of 39.6 L/hr two copper specimens (one of each grade ie; old and new) were also used to measure their free corrosion potential as a function of time.

The flowing rig mentioned above was designed by a final year undergraduate student for his final year project (38). The same flow rig has been used in this work for a few tests which were performed for different grades of copper with a flow rate of 147.6 L/hr except for specimen 1 in figure 30 in which the flow rate was 78 L/hr. The flowing rig was designed in such a manner in which two lengths of copper tube were used as working electrode and counter electrode seperated by a non-conducting material such as PVC. All the specimens used in the flowing rig tests were subjected to anodic polarisation scans. The copper tube sample used in the flowing rig were 200mm long and 28mm of diameter. The photographs shows the flowing rig used in this work.





Photographs shows the flowing rig used for copper specimens in N/ how water.

The results shown in figure 21 demonstrates the performance of old copper [B1] specimens in slowly moving hot tap water (40-46^{o}C) with a flow rate of 23.4 L/hr. Each curve on figure 21 represents an individual specimen exposed for the time shown with out prior polarisation.

In the slowly moving hot tap water a rapid change in free corrosion potential in the positive direction was observed for the specimen after one day of immersion but no such big changes were observed in the free corrosion potential of the other specimens at longer times. The more negative Ecorr observed for specimen 1 may be related to the surface condition of this particular specimen because the Ecorr of old copper specimens in moving cold water were in the range of -150mV to -185mV. The breakdown of protective film occurs at about +60mV for all the specimens with a passive current range of about 2μA-6μA except specimen 1. The increase in current above breakdown potential was about the same for all the specimens except specimen 1 because in case of specimen 1 the increase in current with response to potential was observed from the beginning without any interruption.

The old copper specimens immersed in moving hot tap water attains more noble potential values as compared to old copper specimens with the same immersion time (figure 2) in moving cold water.

The results given in figure 22 shows the performance of new copper specimens [B3] in moving hot tap water (39.6 L/hr) with the length of immersion time.

The results indicate that the breakdown of protective film occurs at about +60mV for the specimen after one day of immersion while this value was about +40mV and +10mV for the specimens after two days and one week of immersion.

The decrease (less positive) in breakdown potential were observed for the new copper specimens in moving hot tap water with respect to immersion time. This decrease in breakdown potential may be related to the effect of temperature on the properties of the developed protective film on the surface of new copper specimens.

The passive current range for the specimen after one day of immersion was about 4μA-5μA while this range for the other two specimens was the same ie 2μA-3μA after two days and one week of immersion.The current response with rise in potential above breakdown was slightly increased with the length of immersion time.

The results shown in figure 23 indicate the trend in free corrosion potential as a function of time for two different grades of copper specimens in moving hot tap water (39.6 L/hr). The results indicate a rapid drift in Ecorr of the specimens in the noble direction between immediate and after one day of immersion.

This change in Ecorr was approximately the same for both grades of copper specimens between immediate and after one day of immersion.

This significant change in Ecorr of both grades of copper specimens provides a backup for the old copper specimens results given in figure 21.

The similarity between the two results was the rapid change in potential in the noble direction in moving hot water after one day of immersion.

Then fluctuations in potential at irregular intervals were observed for both specimens with the length of time but these fluctuations were more obvious in the Ecorr of new copper specimen as compared to the Ecorr of old copper specimen.

This difference in fluctuation in the Ecorr of the new copper specimen may be related to the properties of the developed protective film on the surface of the specimen.

It is evident from the work of Pourbaix (36) in Brussels water that such drops in potential may indicate the periodic local rupture and its refomation in the developed protective film on the surface of the specimens.

The above results indicate a gradual increase in free corrosion potential in the noble direction with response to time for both specimens in moving hot tap water.

The results given in figure 24-26 demonstrate the performance of both grades of copper in moving hot tap water ($44^{o}C$,39.6 L/hr) after 11 months of immersion without prior polarisation. The results in figure 24 shows the anodic polarisation scan for both grades of copper specimens after 11months of immersion while figure 25 and 26 shows the **cathodic** and anodic polarisation scan. The **cathodic** polarisation scans were performed before the anodic polarisation scans.

The anodic polarisation results obtained for both grades of copper (figure 24) after 11 months of immersion indicate that the breakdown of protective film occurs at about +90mV for both grades of copper specimens. The passive current range was about 4μA-5μA for old copper specimen while this value was in the range of about 5μA-6μA for new copper specimen.

The results in figure 25 and 26 indicate the **cathodic** and anodic performance for both grades of copper in moving hot tap water (39.6 L/hr) after 11 months of immersion.

The results indicate a difference of about 50mV in the free corrosion potential of the old copper specimens i.e. negative Ecorr for this old copper specimen was observed as compared to the Ecorr of the old copper specimen in figure 24 after the same immersion time. The Ecorr of the new copper specimens after the same immersion time was not much different i.e. the Ecorr of this specimen (figure 25) was negative by 18mV from the Ecorr of the new copper specimen in figure 24.

In the case of old copper the Ecorr of old copper specimen in moving hot tap water was about 60mV more noble as compared to old copper specimen in moving cold water(figures 10,24). It was found that the free corrosion potential of of new copper specimens was the same in both conditions ie -31mv in moving hot tap water as well as in moving cold water. Both the passive current density and the increase in current above breakdown potential was slightly high for both grades of copper specimens in moving hot tap water as compared to moving cold tap water.

In the succeeding anodic scans, similar breakdown potentials were observed as for the specimens on which an anodic scan alone was done (figure 24). However somwhat higher (8-12 μA) passive current were recorded in those anodic scans carriedout after a cathodic ones. In the **cathodic** polarisation scan very low current was observed for quite high cathodic overpotential for old copper as compared to the **cathodic** polarisation scan of new copper (figure25&26).

In the anodic polarisation scan the increase in current above breakdown potential for both grades of copper were behaving in the same manner.

The results given in figure 27-28 are re-plots of the results from the previous graphs to demonstrate the performance of different grades of copper with the length of time in moving hot water.

The above results suggests a drift in the noble direction of free corrosion potential for both grades of copper.

This drift in potential was rapid between immediate and after one day of immersion in moving hot water as compared to the drift in potential in moving cold water

The potential versus time results in moving hot water indicate approximately a similar drift in Ecorr of both grades of copper between immediate and after one day of immersion.

It has been mentioned eariler in the results of figure 21 in which considerably more negative Ecorr was observed for old copper specimen upon immersion in moving hot water.

This significant negative Ecorr behaviour of the particular specimen may be related to its surface condition which behaves in a different manner from other old copper specimens upon immersion in moving hot water as well as in moving cold water. This reasoning is supported by the initial Ecorr of the other old copper specimen (figure23) upon immersion in moving hot water which was -158mV while the Ecorr of the old copper specimens in moving cold water was in the range of -150mV to -185mV upon immersion.

The results obtained in moving hot water (40-50^{o}C) for different grades of copper shows remarkable similarity at later times in the breakdown potential values and this may be attributed to the developed protective film on the specimens. The above results indicate a gradual increase in potential in the positive direction with response to time for both grades of copper after the rapid drift in the beginning.

This significant change in potential which were observed in the beginning may be related to the effect of temperature on the reaction rate of some active species present in the water.

For instance, if the water contains chlorite ions (ClO^{-}_{2}) which results from the disproportionation reaction in water to which chlorine gas or hypochlorite is added for sterilisation process.

It is evident from the literature (27) that the reduction rate of chlorite ion increases with the rise in temperature.

In a number of cases, the temperature modifies the influence of other corrosion factors i.e.

When the corrosion proceeds with Oxygen depolarization, the increase in temperature accelerates the reaction rate in the usual way while on the other hand the increase in temperature decrease the concentration of Oxygen in the solution. The temperature will increase the corrosion rate in the beginning but later will decrease because of low Oxygen concentration in the solution. In a closed system where the oxygen cannot escape, the increase in temperature will increase the corrosion rate.

It is also evident from the work of Akimov (19) that the temperature will accelerate the corrosion rate if the properties of the developed film are temperature dependent.

It is apparent from the literature on pitting corrosion of copper that type 2 pitting which is a hot water phenomenon rarely occurs below $60^{o}C$ but its mechanism is still not fully understood.

The subsequent gradual increase in potential (figure 23) after the first day in the noble direction with respect to time may be the reason for the corrosion of copper in this water because the avoidance of more noble potential has been suggested by investigators (24,25,35) which is regarded the best preventive method against copper corrosion.

The response of breakdown potential in moving hot water is only apparent for the new copper specimens in figure 22. The decrease (less positive) in this value was observed with the length of immersion time for the specimens in figure 22.

The above results are interesting from the point that similar breakdown potential values were observed for both grades of copper in moving hot water after 11 months of immersion.

Also the increase in current above breakdown potential was the same for both specimens.

The results obtained in moving hot water after 11months shows remarkable similarity to the results obtained in moving cold water after one year in many respect for both grades of copper except the Ecorr of one old copper specimen (figure 24) which was more noble in hot water. Also the increase in current above breakdown potential was slightly high in moving hot water as compared to moving cold water.

The experiments described below were carried out with the rig mentioned earlier in more rapidly flowing hot tapwater with different grades of copper (B3 and B4). The flow rate was 147.6 L/hr throughout the experiments except in one scan (day one of figure 30) which was 78 L/hr.The results shown in figure 29-31 demonstrate the behaviour of different grades of copper in flowing hot tapwater obtained from the rig. The different curves represent seperate experiments involving different specimens exposed for the time mentioned without prior polarisation.

Measured temperatures during this series of tests were in the range of 29-48^{o}C which was a larger range than was hoped for but due to diffculties in controlling the temperature in this rapidly flowing rig.

Figure 29&30 are results obtained on table X copper but obtained from different merchants. The results in figure 29 were obtained on the same source of copper as all the previous described (new copper B3) in polarisation experiments.

Figure 30 represents results on copper from a second merchant and is denoted **B3/B.**

This source of copper was only used for the results shown in figure 30.

The aim behind these experiments for the same grade of copper was to see if there is any difference in the same grade of copper obtained from different merchants.

The results in both figures (29&30) demonstrate that the same grade of copper obtained from different merchants were not behaving in the same manner.

The results indicate a difference of about 100mV in the Ecorr of the **B3/B** specimens compared to B3 and B4 copper specimen obtained from different merchants after one day of immersion but at later times the difference in Ecorr of the specimens was in the range of 10mV to 30mV . Figure 29-31 show that all the grades of copper exhibited passive behaviour in this rapidly flowing water. The breakdown potential during the anodic scan was fairly clearly evident for grade **B3/B** (figure 30) but less so for the other grades (figure 29-31). Nevertheless estimates of Eb were made as follows. For the grade B3, after one day, breakdown potential appears to be about +60mV.

For grade **B3/B,** The breakdown potential values increased progressively from about 0mV after one day to +40mV,+60mV and +70mV for second,third and fourth days respectively. And for the table Y copper (figure 31) breakdown potential appears to be 65mV for 1-3 days.

For all the three grades passive current was in the range 2-5μA where direct comparison is possible between the two different flow rate conditions (i.e. for grade B3), there did not appear to be a great difference in the behaviour although the slower flow rate tests (figure 22) were at a higher temperature (44-50°C).

The results obtained from the flowing rig indicate that not only table Y [B4] copper tube was different from table X [B3] copper tube but also the table X [B3] tube showed different behaviour obtained from different stockiests. The results obtained from the flowing rig are limited but may demonstrates that the same grade of copper is exposed to different conditions in the two places which is responsible for the different behaviour of the same grade of copper. These results suggests that copper is very sensitive to its initial treatment and poor workman ship have to play some role in the corrosion of copper.

Table 4 :- The table shows some of the parameters for both grades of copper in moving hot water.

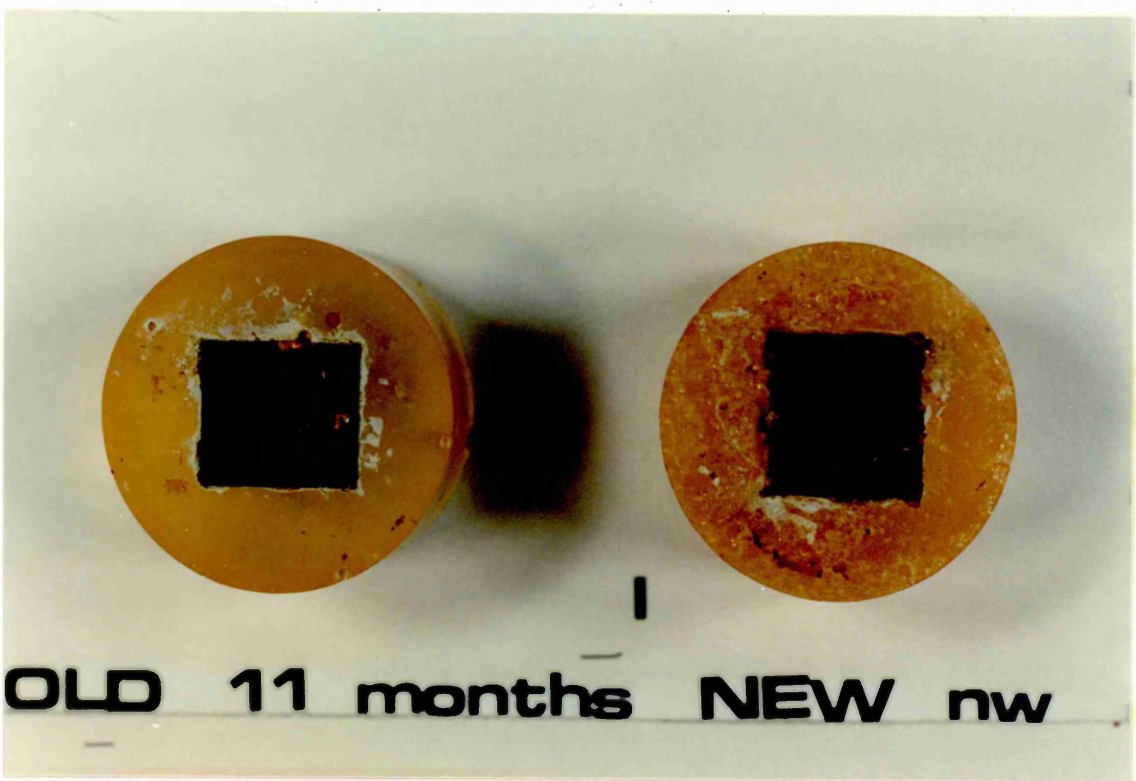
Normal hot tap water

FIGURE AND BATCH NO.	TIME OF IMMERSION DAYS	Ecorr mV	Ebreak mV	Ipassive µA	Iabove Ebreak µA
B1 | 21	IMMEDIATE	-284	-	-	-
	ONE DAY	-19	60	1-2	High
	TWO DAYS	-43.2	60	5-6	Slow
	SEVEN DAYS	-23.5	60	3-4	High
B3 | 22	ONE DAY	-113.5	60	4-5	**slightly increased with time**
	TWO DAYS	-49	40	2-3	
	SEVEN DAYS	-51	10	2-3	
B1 | 24	ONE YEAR Approximately	17, -35	90	4-5	**SAME**
B3		-31, -49	90	5-6	
B3 | 29*	**Flowing rig** *				
	ONE DAY	-41	**60**	**2 - 5**	**Slow**
	TWO DAYS	-17			
	THREE DAYS	-12			
	FOUR DAYS	-14			
	FIVE DAYS	+1			
B3 | 30*	ONE DAY	-131	0	4-5	High
	TWO DAYS	-45	40	3-4	Slow
	THREE DAYS	-21	60	3-4	Slow
	FOUR DAY	-51	70	3-4	Slow
B4 | 31*	ONE DAY	-30	**65**	**4 - 5**	**Slight increased with time**
	TWO DAYS	-11			
	THREE DAYS	-2			

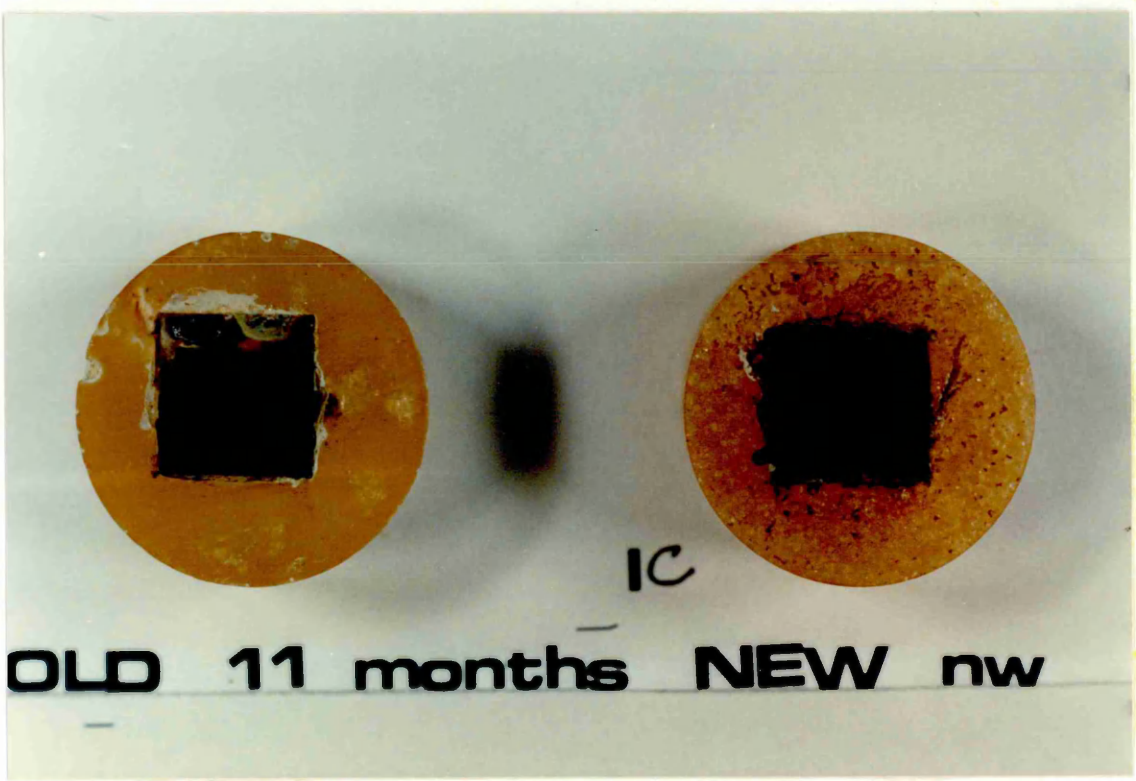
* **Represents the flowing rig work.**

4.3.2. Visual examination

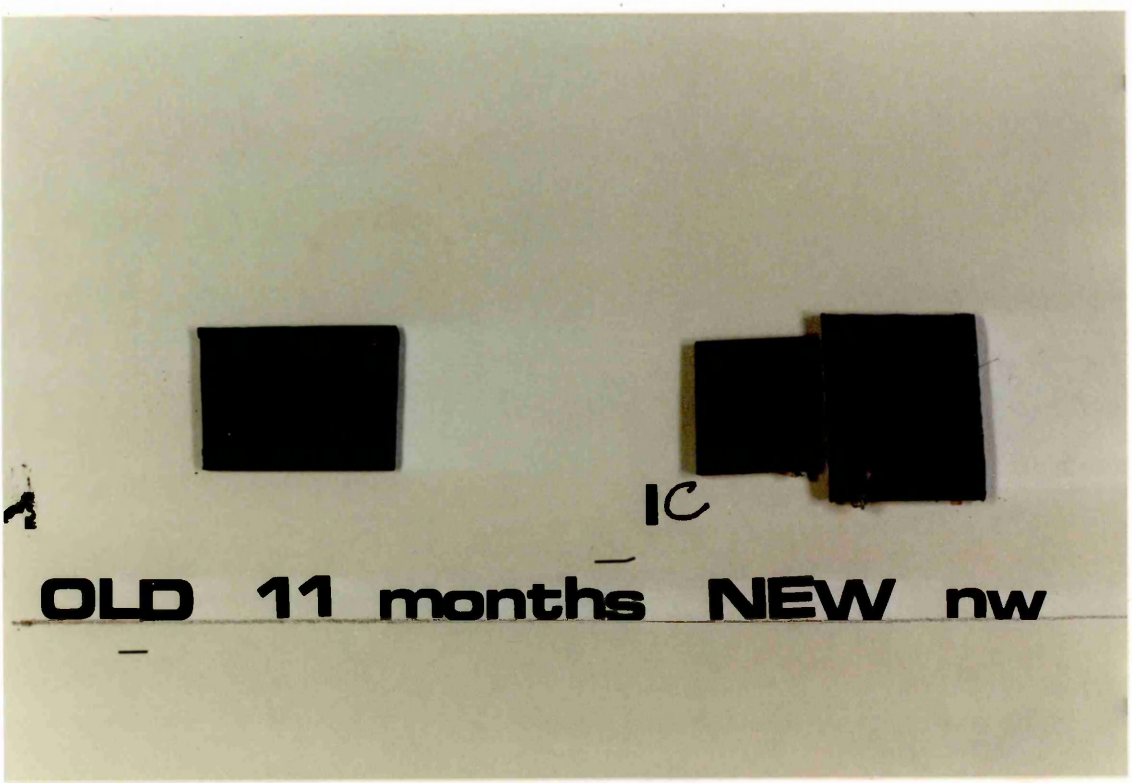
The photographs shown in figure I-Ic shows the surface of copper specimens after 11 months of immersion in normal hot water (40-50^{o}C) . The photograph I represent the copper specimens after anodic polarisation while Ic shows both cathodic and anodic polarisation and also unmounted specimens. Similar corrosion product was observed on all the specimens, ie a black layer was observed on the surface of the specimens underneath the green/brown corrosion product.



Photograph I shows the surface of copper specimens after 11 months in N/H (Anodic scan).



Photograph IC shows the surface of copper specimens after 11 months in N/H (Cathodic&Anodic).



Photograph IC shows the surface of unmounted specimens in normal hot tapwater (11months).

4.4.1. Moving hot water at 60°C

The main concern of the experimental work described below was to look at the performance of two different grades of copper [B1&B3] in slowly moving hot water at 60°C. The flow rate of the water was about 20 L/hr. The tank was receiving normal hot water from the tap (40-50°C) which was then heated upto 60-65°C by another titanium immersion heater with thermostatic control which was fitted in the tank. A number of flat copper specimens were immersed in moving hot water tank at the same time. Some specimens were used to measure their free corrosion potential as a function of time while the others were subjected to polarisation scans over a period of time.

It was very diffcult to pointout the passive current region and breakdown potential for all those specimens subjected to polarisation scans in moving hot water (60°C) because of its active behaviour in this condition as compared to the specimens in moving cold water and moving hot water (40-50°C). In view of the above reason every effort has been made to plot all the anodic polarisation scans on three cycle log paper to get the corrosion current and calculate the corrosion rate for individual specimen. The corrosion current was obtained for all the specimens subjected to anodic polarisation scans but the cathodic scans were ignored due to diffculties in identifying the linear tafel region in the potential verses log current plots. The corrosion current and corrosion rate have been given in table 1 at the end of this section.

4.4.2. Measurements of corrosion rate

Corrosion can be estimated by the corrosion rate under specified environmental condition.

The corrosion rate for the two different grades of copper immersed in moving hot water at $60^{o}C$ have been calculated as follows.

The current I is the rate of charge transfer and the rate of one ampere is equal to one coulomb per second.

1 Faraday => Dissolved 1 equivalent metal

1 Faraday => Atomic weight/Valency

For copper Cu ---- $Cu^{2+} + 2e$

96500 C = 63.54/2 grams of copper

where Atomic weight of Cu = 63.54 grams

96500 amp.sec = 31.77 gm of Cu

I amp => (31.77/ 96500) x I gm/sec

when I = Micro-amperes

then current in amp. = $I \times 10^{-6}$

Area of the specimen = 1 cm^2

Density of copper = 8.96 gm/cm^3

$$\text{Thickness loss} = \frac{31.77 \times I \times 10^{-6}}{96500 \times \text{area} \times \text{density}} \text{ cm/sec} \quad \text{- - - - B}$$

Thickness loss in cm/year = B .60.60.24.365 cm/year ---- Z

$$B = \frac{31.77 \times I \times 10^{-6}}{96500 \times \text{area} \times \text{density}} \text{ cm/sec}$$

Thickness loss mm/year = Z x10 mm/year

where 1cm = 10 mm

Corrosion rate was calculated for copper specimens after immersion where current was 14μA as follows.

Corrosion rate = (31.77x14x10^{-6}x60x60x24x365) /96500x 8.96

Corrosion rate = 0.016 cm/year

Corrosion rate = 0.16 mm/year

The results given in figure 32-34 demonstrate the performance of both grades of copper about one hour after immersion in moving hot water at 60°C. In the anodic polarisation (figure 32), the increase in current were observed for both specimens without interruption with response to potential.

The results indicate a clearly active behaviour of the specimens after immersion. The calculated corrosion rate for both specimens by the above method was about 0.16mm/year and .17mm/year respectively.

Figure 33-34 shows both anodic and cathodic polarisation for both grades of copper specimens. The cathodic polarisation scan was performed before the anodic polarisation scan in both cases. In the cathodic polarisation scan a peak was observed for both grades of copper specimens in the potential range of about -70mV to -150mV from Ecorr for new copper while this range was about -50mV to -130mV for old copper. This peak was more obvious in the cathodic polarisation scan of new copper specimen as compared to old copper specimen. This peak will be discussed later in this section in the light of previous observation by one investigator.

The results given in figure 35-35a indicate the trend in free corrosion potential as a function of time for both grades of copper [B1&B3] in moving hot water (60°C). The potential of both copper specimens with respect to time were recorded in two different stages due to the following reasons.

One potential problem that came to light in moving hot water ($60^{o}C$) was the use of agar saltbridge.

The saltbridge worked perfectly under moving cold water and normal hot water ($40\text{-}50^{o}C$) condition but in hot water at $60^{o}C$, the agar tended to liquefy and air bubbles were created in the tubes. This meant that saltbridge had to be renewed frequently which was a time consuming process.

The second reason for this gap was to see wether at longer times the potential was behaving in the same manner as were observed in the first two weeks or behaving differently.

The results indicate (figure35) a gradual increase in the free corrosion potential in the first period of about two weeks without any fluctuation as were observed for both grades of copper specimens in moving cold and normal hot water ($40\text{-}50^{o}C$) (figures 4,23). After four months of interval the potential was again measured for about two weeks. The fluctuations in free corrosion potential of both specimens were observed in a small scale as compared to the fluctuation of copper specimens in moving cold and normal hot tap water ($40\text{-}50^{o}C$). One of the investigator has suggested (35) that these fluctuations in potential may indicate the periodic local rupture and reformation of the protective film on the surface of the specimens.

The results given in figure 36 shows the behaviour of old copper [B1] in moving hot water ($60^{o}C$). Each curve on figure 36 represents an individual specimen exposed for the time shown without prior polarisation. As it is obvious from figure 32 that both grades of copper were clearly active upon immersion in moving hot water ($60^{o}C$).

These results also indicate that passive behaviour was still not observed after one day although, after the second day, the anodic polarisation curves were becoming steeper indicating a possible move towards passive behaviour. The calculated corrosion rate for all the specimens was about .07 mm/yr,.08 mm/yr,.03 mm/yr and .04 mm/yr respectively.

The results given in figure 37 shows the performance of both grades of copper after one week of immersion without prior polarisation. The specimens showed some passive behaviour after one week as compared to the specimens upon immersion (figure32).

In comparing the old copper specimen after one week of immersion with the old copper specimen after 3 and 4 days of immersion (figure 36), it was observed that the specimen after one week of immersion was slightly active than the specimens after 3 and 4 days of immersion. The other interesting point was that approximately similar Ecorr were obseved for both grades of copper after one week of immersion.

Also the results indicate that the performance of new copper [B3] was slightly better than the performance of old copper after one week of immersion. This difference may be due to the surface layer formed on the specimens which produce this slight change in the behaviour of both grades of copper. The calculated corrosion rate for old copper specimen after one week of immersion was .06 mm/yr. The corrosion rate for new copper specimen was about .03mm/yr which was decreased after week as compared to the corrosion rate of the specimen after immediate immersion.

This decrease in corrosion rate also give an indication for the formation of corrosion product on the surface of the specimens with the length of time which may be the reason for such decrease in the corrosion rate.

The results shown in figure 38 indicate the performance of both grades of copper after five months of immersion in moving hot water without any prior polarisation.

The results indicate that the performance of new copper specimen was again slightly better than old copper specimen because of some passive behaviour (pseudo passivation) which was observed for new copper specimen as compared to old copper specimen. Also the rapid increase in current was observed for new copper specimen in the potential range of about +140 mV as compared to old copper. The results indicate that the specimens are trying to exhibit some passive behaviour due to the formation of surface layer formed on the specimens with the length of time. The existance of surface layer on the specimen with time can easily be judged by comparing the specimens with different immersion time (figures 32,37&38). The calculated corrosion rate for old and new copper specimens was about .06 mm/yr and .03 mm/yr after five months of immersion.

The results given in figure 39-41 shows the performance of both grades of copper approximately after one year of immersion without any prior polarisation in hot water. The results indicate (figure 39) that the performance of old copper specimens seems to be slightly better than the performance of new copper specimens.

In view of the above change, the results suggests that changes may occur in the corrosion product layer with the length of time because of the different relative behaviour observed for both grades of copper after five months and after one year of immersion and the specimens were still not passive. The calculated corrosion rate for old and new copper specimen was about .09 mm/yr and .05 mm/yr respectively.

The results in figure 40-41 shows both the anodic and cathodic behaviour of both grades of copper after one year of immersion without prior polarisation. The cathodic scan was performed before the anodic scan. In the cathodic scan similar peaks were observed for both specimens after one year as were observed for the specimens after immersion.

The potential range in which the peak were observed was decreased (more positive) with the length of time. In the cathodic scan of new copper the peak was observed in the potential range of about +33mV to -30mV while this range was about +40mV to -40mV for old copper.

This decrease in peak potential range may be related to the difference in the Ecorr of the specimens because the Ecorr of the specimens after one year was positive as compared to the Ecorr of the specimens after immersion.

The results shown in figure 42-43 are re-plots of the results from the previous graphs to demonstrates the overall performance of both grades of copper with respect to time in moving hot water at $60^{o}C$.

The above results suggests that specimens attains more noble potential upon immersion in hot water at 60°C as compared to the specimens on immersion in normal hot water (40-50°C) and in moving cold water. Also in hot water at 60°C, clearly active behaviour were observed for the specimens upon immersion (figure 32) as compared to the specimens upon immersion in the other two conditions i.e. normal hot water and moving cold water (figures 4,23).

The results obtained for the specimens in the three different conditions (moving cold water,normal hot water and hot water at 60°C) suggest that the increase in electrode potential (more positive) and active behaviour were observed for the specimens with rise in temperature. These results provide a sound base for the effect of temperature on copper specimens which may be the reason for the corrosion of copper in the water of this locality.

It is evident from the literature (24,35) that the avoidance of more noble potential is regarded the best preventive method against copper corrosion.

The second effect of temperature i.e. active behaviour of the specimens with rise in temperature may be related to the quality of water and the composition of corrosion product layer.

There is some evidence from the literature (27) on the effect of temperature on the corrosion of copper when the water contains such sort of active species like chlorite ions (ClO^-_2) which results from the disproportionation reaction in water to which chlorine gas or hypochlorite is added for sterilisation process.

They have observed that the reduction rate of chlorite ions increases with the rise in temperature which effect the electrode potential of copper.

It is also evident from the literature (11,24,27) on type 2 pitting of copper which is a hot water phenomenon and this type of attack is highly dependent on the quality of water.

Akimov (19) has suggested that temperature can effect the corrosion of copper in that sense when the properties of the corrosion product layer are temperature dependent. The composition of corrosion product layer and its properties are not fully understood due the lack of time at this stage of study.

In hot water ($60^{o}C$) the second change was noticed in the potential time curve (figure 35-35a) for both grades of copper. The results indicate that no frequent fluctuations in potential were observed for the specimens in hot water at $60^{o}C$ as compared to the fluctuations in potential of the specimens in normal hot water and in cold water (figures 4,23).

This difference in fluctuation of potential may be related to the periodic local rupture and re-formation of the surface layer.

In hot water at $60^{o}C$, perhaps the re-formation may take longer time after the rupture occurs as compared to normal hot water and cold water. This longer time for the re-formation of surface layer may be related to the influence of temperature on the properties of the corrosion product layer.

In hot water ($60^{o}C$) a peak was observed for both grades of copper in the cathodic scan. The potential range in which the peak was observed decreased with the length of time.

This decrease in the peak potential range may be related to the differences in the free corrosion potential of the specimens with the length of immersion time. The peak in cathodic scan suggests the presence of some active species in the water or in the corrosion product layer which is responsible for such chang in the cathodic scan.

Suzuki et al (27) has observed similar peak in the cathodic scan for one copper sample in water containing 100 ppm of sodium hypochlorite (NaClO). They have suggested that such peak in cathodic scan results from the reduction of compounds accumulated in the corrosion product layer.

All this experimental work demonstrates the performance of copper in simple water without the addition of any oxidising agent.

Table 5:- The table shows some of the values for both batches of copper in moving hot water at 60 deg-C.

Moving hot water at 60 deg-C

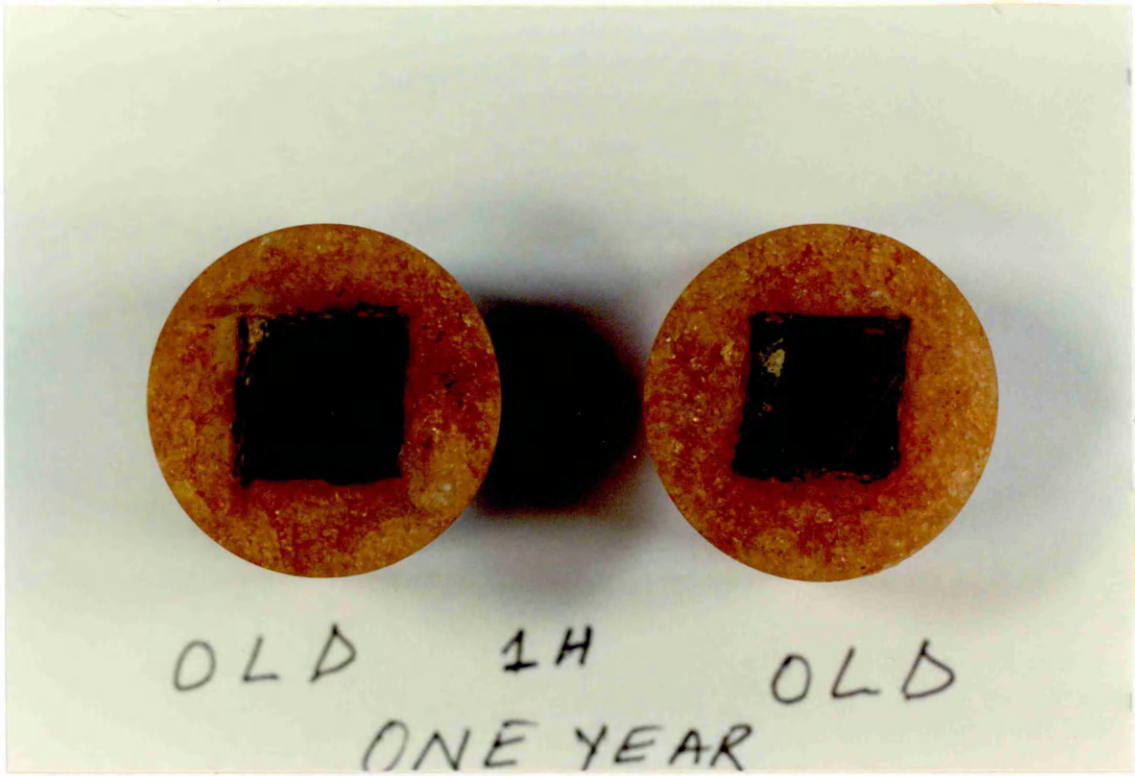
FIGURE AND BATCH NO	TIME OF IMMERSION DAYS	GRADIENT mV/ decade	CURRENT µA	CORROSION RATE mm/ year
B1		38	14	0.16
32	IMMEDIATE			
B3		48	15	0.17
B1 36	ONE DAY	45	6.4	0.07
	TWO DAYS	68	7.3	0.08
	THREE DAYS	52	3	0.03
	FOUR DAYS	69	3.3	0.04
B1		34	5	0.06
37	SEVEN DAYS			
B3		50	2.7	0.03
B1		39	5.4	0.06
38	150 DAYS			
B3		50	2.6	0.03
B1		62	8	0.09
39	ONE YEAR			
B3		25	4.6	0.05
B1 40*	ONE YEAR	**64**	**5**	**0.06**
B3 41*	ONE YEAR	**90**	**8**	**0.09**

Note:- * **represents those specimens on which cathodic scan was performed before anodic scan.**

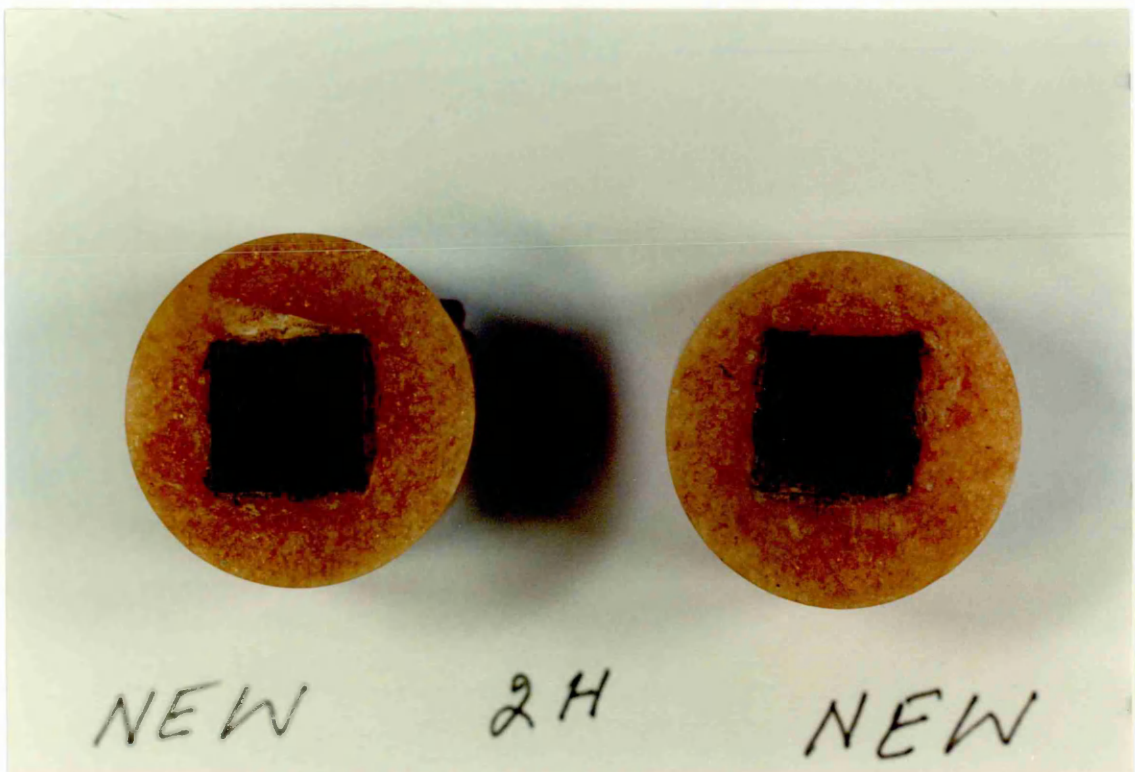
4.4.3. **Visual examination**

The photographs in 1H-2H shows the copper specimens after one year of immersion in hot water at 60°C. The 1H shows old copper (B1) while the 2H represents the new copper (B3). The specimens given on the left represents the specimens subjected to anodic polarisation while the right side shows the specimens subjected to both cathodic and anodic polarisation.

Similar corrosion product was observed on these specimens in hot water at 60°C as were observed in normal hot water, i.e. a black layer was observed underneath the green/brown corrosion product. On two unmounted copper specimens (one of each grade) some small spots were observed which may be indicating the initiation of pits on these specimens.

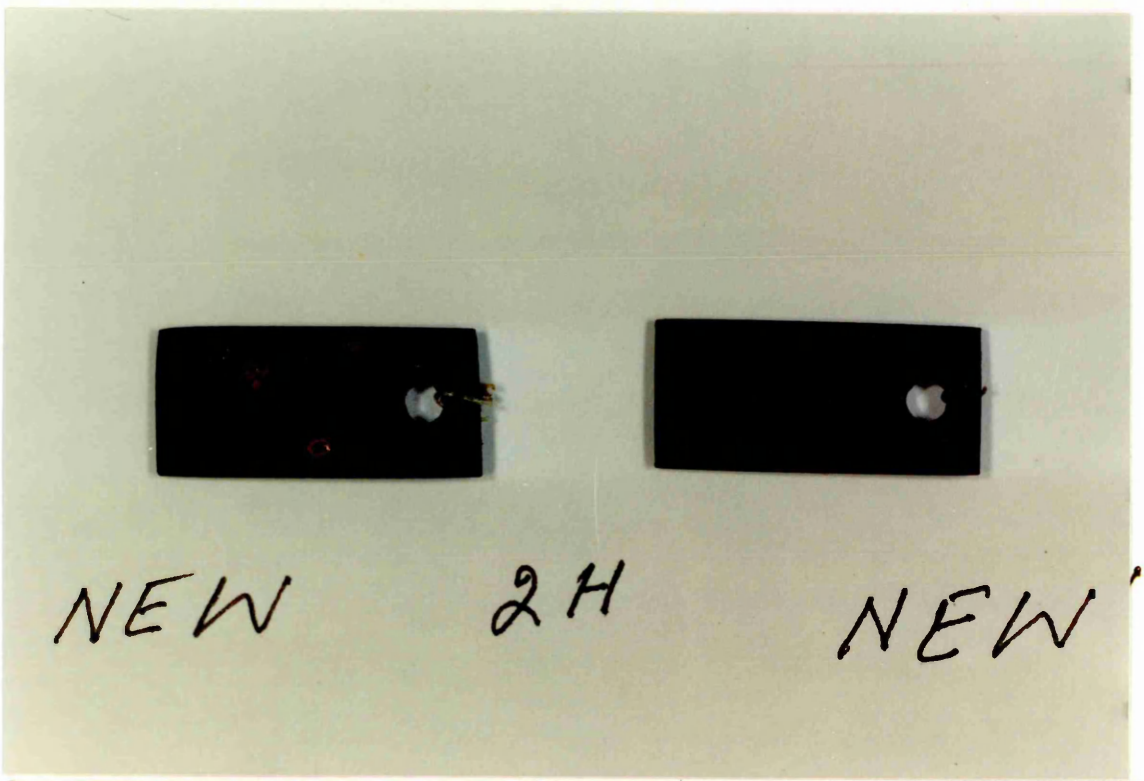


Photograph 1H shows the surface of old copper specimens after one year in H/W(60) Left anodic



Photograph 2H shows the surface of new copper specimens after one year in H/W(60) Left Anodic

Photograph 1H shows the surface of unmounted old copper speciemens after one year. [H/W 60]



Photograph 2H shows unmounted new copper specimens after one year in hot water (60).

4.5.1. POTENTIAL HOLDING EXPERIMENTS

The aim of these experiments was to investigate the response of current by holding the potential of copper specimens above free corrosion potential and also with respect to time and temperature. The effect of abrasion on the specimens free corrosion potential has also been studied. In some experiments the potential of the specimen was held at +150mV which is the critical potential value for copper suggested by other investigators (24) in cold and hot water while in other cases the potential was held at a less positive value(+40mV,30mV). In another set of experiments the potential was held at that value when the current was reached to 1μA or 2μA.

The first study was conducted in Glasgow and in Lancashire water on new copper specimens obtained from a merchant (BS 2871) in this connection. The potential of both copper specimens was held at +150mV and recorded the current response with time for twenty days. The current of the copper specimen in Glasgow tap water was higher for the first two days than the current of the specimen in Lancashire water. On the third day of the experiment a sudden decrease in current was observed for the specimen in Glasgow tap water while the decrease in current for the specimen in Lancashire water was comparatively slow.

The results of these specimens are given in figure 44 which indicate that this decrease in Glasgow water may be due to the formation of a film on the surface of the specimen which is responsible for such reduction in current as compared to Lancashire water.

The decrease in current is clear for both specimens with the length of time but was fluctuating rather more in Lancashire water than in Glasgow water.

The currents in these experiments were extremely high. Consequently, further experiments were carried out at less positive potentials.

The second study was performed for new copper specimens in Glasgow tapwater to see the relation of current with temperature. The potential of both specimens were held at different potential values. The potential of specimen 1 was held at +40mV while the potential of specimen 2 was held at that value where the current reached to 2μA. The current was recorded for both specimens with respect to temperature as given in figure 45. These results are interesting from one aspect that the increase in current with rise in temperature was observed for both specimens which was higher for specimen 1 from the beginning as compared to specimen 2. This difference in current increase may be related to the value at which the potential was held for the specimens. The potential of specimen 1 was held at more positive value as compared to specimen 2.

These results demonstrate the important and stimulant role of temperature in the corrosion of copper at higher values.

Similar study was performed for other two copper specimens. The potential of both specimens were held at 30mV above Ecorr and recorded the current response with rise in temperature. The results in figure 46 also indicate that temperature may be a factor in stimulating the corrosion rate of copper.

Akimov (19) has studied the influence of temperature in the corrosion process.

He suggested that in a number of cases the change of temperature modifies the influence of other corrosion factors. He found that the rise in temperature acts in two different ways when the corrosion proceeds with Oxygen depolarization. The increase in temperature will accelerate the corrosion rate in the usual way but also decrease the concentration of Oxygen in the solution which tends to decrease the corrosion rate with further rise in temperature. In a closed system where the Oxygen cannot escape, the rise in temperature will increase continously the corrosion rate. He also suggested that if the properties of the film are temperature dependent, the change in corrosion rate can be be attributed to temperature.

In the second investigation the effect of temperature on the electrode potential of copper in Japanese water has been studied by Suzuki et al (27). They have found that the reduction rate of chlorite (ClO^-_2) ion was increased with rise in temperature which was responsible for the rise in electrode potential. Oxyacids and oxyanions of chlorine formed in water to which chlorine gas or hypochlorite was added for sterilization process.

Therefore these results demonstrate that the role of temperature must not be ignored in the corrosion of copper in this water. Perhaps there may be the possibility of some substances present in the water or in developed protective layer which is sensitive to temperature and stimulate the corrosion of copper in this locality.

Further experimental work was carried out to see the current response with respect to time.

The aim behind this study was to ensure that the increase in current was due to temperature in the previous experiments and not due to time. The potential of new copper specimen was held 30mV above Ecorr and left for few hours to see wheather the current is increasing with time or not.

The result given in figure 47 indicate that temperature was the only factor responsible for the increase in current and not the time in the previous experiments [figure 45&46].

The results given in figure 48 shows the influence of temperature on the free corrosion potential of two copper specimens. Both copper specimens were first immersed in Glasgow tapwater and then the temperature was raised to see its influence on the Ecorr of the specimens. The results indicates that the free corrosion potential of both specimens with the rise in temperature were fluctuating in a little different manner from each other.

These fluctuation in Ecorr of specimen 1 with the rise in temperature has been observed more frequently as compared to specimen 2. Similar variation in Ecorr for other specimens in moving hot water in the polarisation experiments with the length of time has been observed which has been discussed eariler in this chapter.

Next these three experiments were carried out on the hope to make clear these variation in free corrosion potential each time after grinding upto possible range which were noticed during the polarisation experiments. The specimens were first abraded each time and then immersed in the water. The specimens were then left in the water for 30 to 40 minutes because of its Ecorr settlement.

This process has been repeated for every specimen each time. The water sample was re-freshed each time for the specimen the result of which is shown in curve 1&2 of figure 49 while the water sample was not re-freshed each time for the other two samples.

These results given in figure 49 demonstrates that these fluctuation may be due to the variation in composition of copper with thickness.

These results are irreproducible but do indicate the possible variation in the condition of copper with thickness of the pipe wall.

It is also apparent from the results obtained from the flowing rig in hot tap water in which different behaviour were observed for the same grade of copper obtained from different merchants which has been discussed in the normal hot water section earlier.

The variation observed in the free corrosion potential after grinding in this work also provides a backup to the work of a final year undergraduate student (38). He noticed that the same grade of copper was not behaving in the same manner. He suggested that such behaviour in the same grade of copper may be related to the changes in the composition of copper which varies with thickness.

4.6.1. COMPARISON OF TWO DIFFERENT WATERS

The main objective of the experimental work mentioned below was carried out in order to look at the behaviour of copper in water of two different localities ie Glasgow vs Lancashire. This was a simple way of judging the aggressiveness of Glasgow water as compared to Lancashire water. All the comparative studies were performed in stagnant condition, but with different temperatures (Ambient, 50°C and 60°C). Also it is worthwhile for mentioning that Oxygen and Nitrogen gas was also bubbled in a few cases to see their influence on the performance of copper.

The first experiment which was performed in cold water with old copper (Specimens made from a tube sample obtained from a hotel) indicate that the specimen attain a little more noble potential immersed in Glasgow water as compared to Lancashire water given in figure 50. In this work, it has been assumed that the potential at which the measured current starts to increase relatively rapidly (compared to prior potentials) represents the onset of protective film breakdown. The results indicate that the breakdown of protective film occurs at about 50mV in Glasgow water while it occurs at about 0mV in Lancashire water. The passive current was in the range of about 4μA-5μA for the specimen in Glasgow water while this value was in the range of about 8μA-9μA for the specimen in Lancashire water. The increase in current above breakdown potential was high in Lancashire water as compared to Glasgow water. The pH of fresh Glasgow tap water always lies in the range of 7-8.5. There was a slight difference in the pH of both waters.

In view of the above reason the Glasgow water was first taken in a beaker and left open to the atmosphere for six hours to drop its value of pH.

In the second study the water was heated upto 50°C to get a situation of normal hot tap water as shown in figure 51. The copper specimens were immersed in water after heating to 50°C. The potential at which the film break down occurs was this time about 30mV and 50mV in Glasgow and Lancashire water respectively. The passive current was in the range upto about 4μA-5μA and 6μA-7μA for both specimens respectively. The results indicate that the increase in current with respect to potential was high in Glasgow water rather than in Lancashire water. Again the free corrosion potential was more noble for the specimen in Glasgow water (as was in cold water). The pH value of Glasgow water was 7.19 (neutral) while the pH of the Lancashire water was in the acidic range (6.65) at the time of experiment.

In the third experiment the water was heated upto 65°C to match the condition of a very hot water given in figure 52. The break down potential was about 90mV for the specimens in both waters. The passive current range was about 9μA-10μA in Glasgow water while this range was about 10μA-12μA in Lancashire water. The results indicate that the increase in current with response to potential was slow in the beginning in both waters but was high later in the Lancashire water as compared to Glasgow water.

4.6.2. EFFECT OF DEAERATION

The influence of Nitrogen gas has been studied on the performance of copper in two different conditions i.e. cold water at ambient temperature and at 60°C. The aim of this was to see the role of Oxygen in the corrosion process.

The results shown in figure 53 demonstrate the behaviour of copper in both waters at ambient temperature involving the bubbling of Nitrogen gas for one hour. The pH of both waters was raised to about 9 (alkaline) by bubbling of Nitrogen gas. The results indicates that the break down of the protective film occurs at about 0mV for the specimen immersed in Glasgow water while this value was about -30mV for the specimen in Lancashire water has shown very similar behaviour in the both waters. Another interesting feature of the experiment was the very low passive current which were observed in both waters, to make this aspect clear , the data on figure 53 is replotted on figure 53A. The increase in current above the breakdown potential was high in Lancashire water as compared to Glasgow water.

The results given in figure 54 shows the performance of copper specimens in both waters heated upto 63°C with the bubbling of Nitrogen gas for one hour.

The results indicate that the break down of the protective film occurs at potential about -20mV in Glasgow water while this value was about 20mV in Lancashire water. The passive current was in the range of about19μA-20μA for the specimen in Glasgow water while this was in the range of about 20μA-22μA in Lancashire water.

The increase in current with respect to potential was slow above break down potential in Lancashire water as compared to Glasgow water

All the copper specimens used in the above experiments were made from a copper tube (sample) collected from a hotel.

The new copper was introduced in the remaining comparison work which was obtained from a local stockiest and confirmed to BS 2871. The results given in figure 55 describes the performance of this new copper in both waters with bubbling of Nitrogen gas for one hour at ambient temperature.

It may also be pointed out that new copper specimens on immersion in both waters exhibit more negative free corrosion potential values as compared to the Ecorr of old copper.

The Ecorr in Lancashire water was 100mV more negative than in Glasgow water. Such negative behaviour of new copper upon immersion as compared to old copper has also been observed in the cold water experiments which been discussed ealier. This change may be related to the metallurgical properties of the new copper material and perhaps the material will lose such property in the exposed environment with the length of time.

The break down potential value observed for the new copper specimens immersed in Glasgow and in Lancashire water were about -40mV and -20mV respectively. Again the passive current densities in this experiment were very low [fig:55A].

The increase in current with response to potential above break down was higher in Glasgow water as compared to Lancashire water.

The study performed in hot water at 63°C with the bubbling of Nitrogen gas for one hour demonstrates the behaviour of new copper specimens in such condition as given in figure 56 and very similar behaviour were observed in the two waters. The break down potential was about 20mV for the specimen in Glasgow water as well as in Lancashire water. The corresponding passive current values were in the range of about 11μA-12μA for the specimen in Glasgow water while this range was about 9μA-10μA for the specimen in Lancashire water. The Nitrogen gas was bubbled in the above experiments in order to decrease the quantity of Oxygen in both waters and see its influence on the free corrosion potential and break down potential of the specimens made from both grades of copper in different conditions i.e. water at ambient temperature and at 60°C.

The effect of deaeration on the free corrosion potential was observed for the specimens made from old copper (sample) as shown in figure 53 and 54.

The specimen attains more negative Ecorr values due to deaeration which was not the case for the specimens without deaeration [50, 51 and 52]. The more negative Ecorr behaviour with deaeration have also been observed for the specimens made from new copper obtained from a stockiest (BS 2871) because the Ecorr of the new copper specimens used in the cold water experiments (without deaeration) was in the range of 230mV to 270mV in cold water.

4.6.3. EFFECT OF AERATION

The results given in figure 57 and 58 describes the performance of both grades of copper at ambient temperature with bubbling of Oxygen for one hour in Glasgow and in Lancashire water.

The results in figure 57 indicate the significant difference between two batches of copper. Thus the free corrosion potential of new copper is considerably more negative. The breakdown of protective film occurs for both grades of copper at about -20mV and about 50mV respectively. The corresponding passive current was in the range of about 6μA-8μA for both specimens.

The increase in current with response to potential above break down was higher for old copper specimen as compared new copper specimen.

Similar trends were observed in Lancashire water [figure 58}. The break down potential value for the specimens immersed in Lancashire water were lies in the range of about 0mV and 40mV for both specimens. Somewhat higher passive current in the range12μA-16μA were observed for the specimens immersed in Lancashire water. The increase in current with response to potential above break down was higher for old copper specimen rather than new copper specimen.

Finally these experiments in figure 59-60 were carried out for both grades of copper in both waters at high temperature involving the bubbling of Oxygen for one hour. The results indicate significant changes in Ecorr between ambient and 63^{o}C for the specimens immersed in Glasgow water in that Ecorr for both specimens was more negative at high temperatures.

In figure 59 the breakdown of protective film occurs at about 0mV for old copper in Glasgow water. The breakdown potential value for new copper specimen is not clear but has been assumed at about -100mV.The passive current was in the range of about 8μA-9μA and about 8μA-16μA for old and new copper specimens respectively.

In figure 60 the breakdown of protective film occurs at about 0mV and about -10mV for both specimens in Lancashire water. The passive current was in the range of 14μA-18μA for old and new copper specimens.

All the results described above demonstrates the performance of both grades copper [B1&B2] in three different conditions at different temperatures in both waters i.e. simple water,deaerated water and aerated water at ambient, 50°C and 60°C.

The above results suggests that the specimens attain more noble potential on immersion in Glasgow water as compared to Lancashire water at all temperatures.

In simple water the decrease in Ecorr (more negative) for the specimens immersed in Lancashire water were observed with response to temperature but the Ecorr of the specimens in Glasgow water behaving in a little different manner.

The value of Ecorr for the specimens immersed in Glasgow water was not shifting constantly either in positive or negative direction (as was the case in Lancashire water) but were slightly fluctuating.

In addition an increase in breakdown potential (more positive) values were observed for the specimens in Lancashire water with rise in temperature.

In case of Glasgow water the breakdown potential value was decreased (less positive) for the specimen from ambient to 50°C and an increase in this value was observed with the rise in temperature from 50°C to 60°C.

The more noble free corrosion potential behaviour of copper specimens on immersion in Glasgow water may be the reason for the corrosion of copper in this locality. Fujii and his colleagues (24) have suggested that regardless of the types of pitting, the avoidance of more noble potential is regarded the best preventive method against copper corrosion.

In the deaerated water the results demonstrate that both grades of copper attain more negative free corrosion potential especially the old copper specimens which were not the case in simple water of both localities.

Also the increase in free corrosion potential (more positive) were observed for both grades of copper specimens with rise in temperature in both waters in the deaerated condition.

In the deaerated Glasgow water the breakdown potential of both grades of copper specimens [B1&B2] were not behaving in the same way with temperature. The breakdown potential of old copper specimen was decreased (less positive) with rise in temperature while the increase in breakdown potential value (more positive) with temperature was observed for new copper specimens.

The breakdown potential of both grades of copper specimens immersed in Lancashire water were behaving in the same manner i.e. an increase (more positive) in this value were observed with rise in temperature.

In the aeration condition the results indicate a significant difference between two batches of copper immersed in both waters except the results of the specimens in figure 59. In figure 59 significant changes in Ecorr of the specimens between ambient and 63°C were observed in Glasgow water, i.e. more negative Ecorr were observed at higher temperatures. The effect of aeration on the breakdown potential value of old copper is apparent, i.e. increased (more positve) in Glasgow water with rise in temperature while the breakdown potential value was the same for old copper specimens in Lancashire water at ambient and 63°C.

The breakdown potential of new copper specimen decreased (less positive) in Lancashire water while the breakdown value for new copper specimen in Glasgow water is not clear.

The aim behind deaeration and aeration was to see the influence of Oxygen on the performance of both grades of copper specimens in both waters.

The above results demonstrate that the specimen attains more negative free corrosion potential in the deaerated water as compared to aerated water.

The influence of Oxygen has been studied by Akimov (19). He suggested that the dual role of Oxygen must not be ignored in the corrosion process.

It acts as a stimulant in the corrosion process that it is a good cathodic depolariser and at the same time an inhibitor when it improves the stability of the protective film. It is also evident from the work of Akimov that oxygen can only act as a stimulant for the noble metals such as copper because of their high chemical stability.

The increase in pH value was observed (alkaline) with the bubbling of Nitrogen gas which may provides the condition for the formation of a protective film. The tendency of pitting corrosion decreases with the increase in pH (18).

The decrease in (less positive) free corrosion potential with rise in temperature may be related to the properties of the developed protective film. The influence of temperature has been suggested by Akimov when the properties of the protective film are temperature dependent.

Suzuki et al (27) has observed the affect of temperature on the reduction rate of chlorite ions (ClO^-_2) which results from the disproportionation reaction in water to which chlorine gas or hypochlorite is added for sterilisation process. The reduction rate of chlorite ions increases with the rise in temperature.

However, the condition for the formation of a protective or non-protective film or the properties of the film is not fully understood in this water at this stage of study.

The table 1 shows the values of different parameters for the both grades of copper specimens in both waters.

Table 6:- The table shows different values for both grades of copper in both waters at different temperatures under different conditions ie, simple water, deaerated and aerated water.

Glasgow water verses Lancashire water

FIGURE AND BATCH NO	Ecorr IN GLASGOW mV	Ecorr IN LANCASHIRE mV	Temp. IN deg-C	Ebreak in Glasg. mV	Ebreak IN Lancas. mV	Ipassi. IN Glasg. μA	Ipassi. IN Lanca. μA	I above Ebreak G	I above Ebreak L
50 B1	-51	-75.5	Ambient	50	0	4-5	8-9	Slow	High
51 B1	-25.4	-87	46-50	30	50	4-5	6-7	High	Slow
52 B1	-45.6	-95	60-63	90	90	9-10	10-12	Slow	High
Deaertion 53 * B1	-232	-266	Ambient	0	-30	7-8	13-14	Slow	High
54 * B1	-144	-160	63	-20	20	19-20	20-22	Slow	High
55 * B2	-338	-432	Ambient	-40	-20	5-6	4-5	High	Slow
56 * B2	-284	-281	63	20	20	11-12	9-10	Slow	High
Aeration 57 * B1	-63	----	Ambient	-20	---	5-6	---	High	---
B2	-230	----		50	---	7-8	---	Slow	---
58 * B1	---	-58.5	Ambient	---	0	--	10-12	--	High
B2	---	-236		---	40	--	15-16	--	Slow
59 * 60 * B1	-156	-61	63	0	0	8-9	13-14	High	High
B2	-281	-151		-100	-10	14-15	17-18	Slow	High

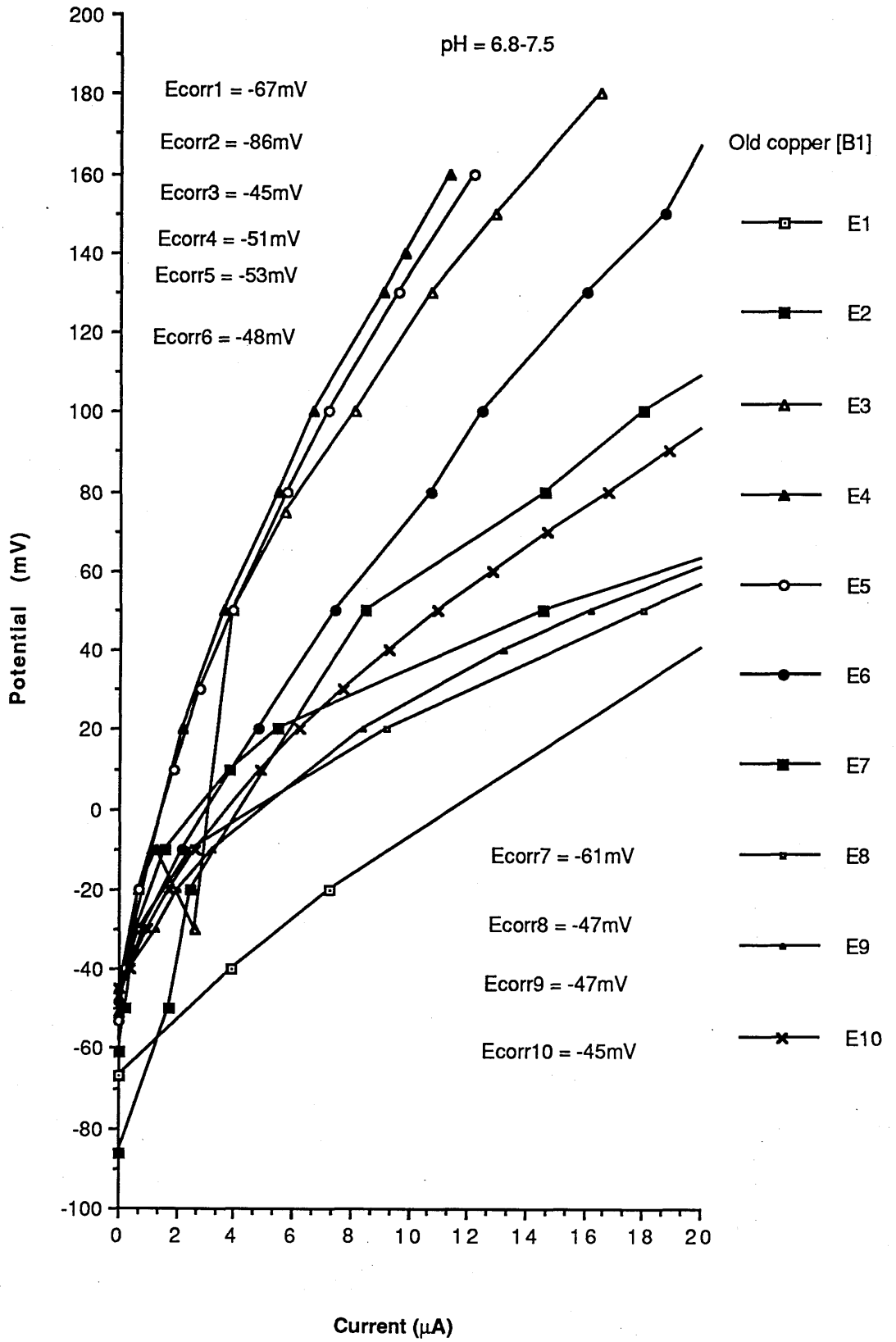
Note:- * represents deaerated condition.
*** represent aerated condition.**

Stagnant condition

Figure 1

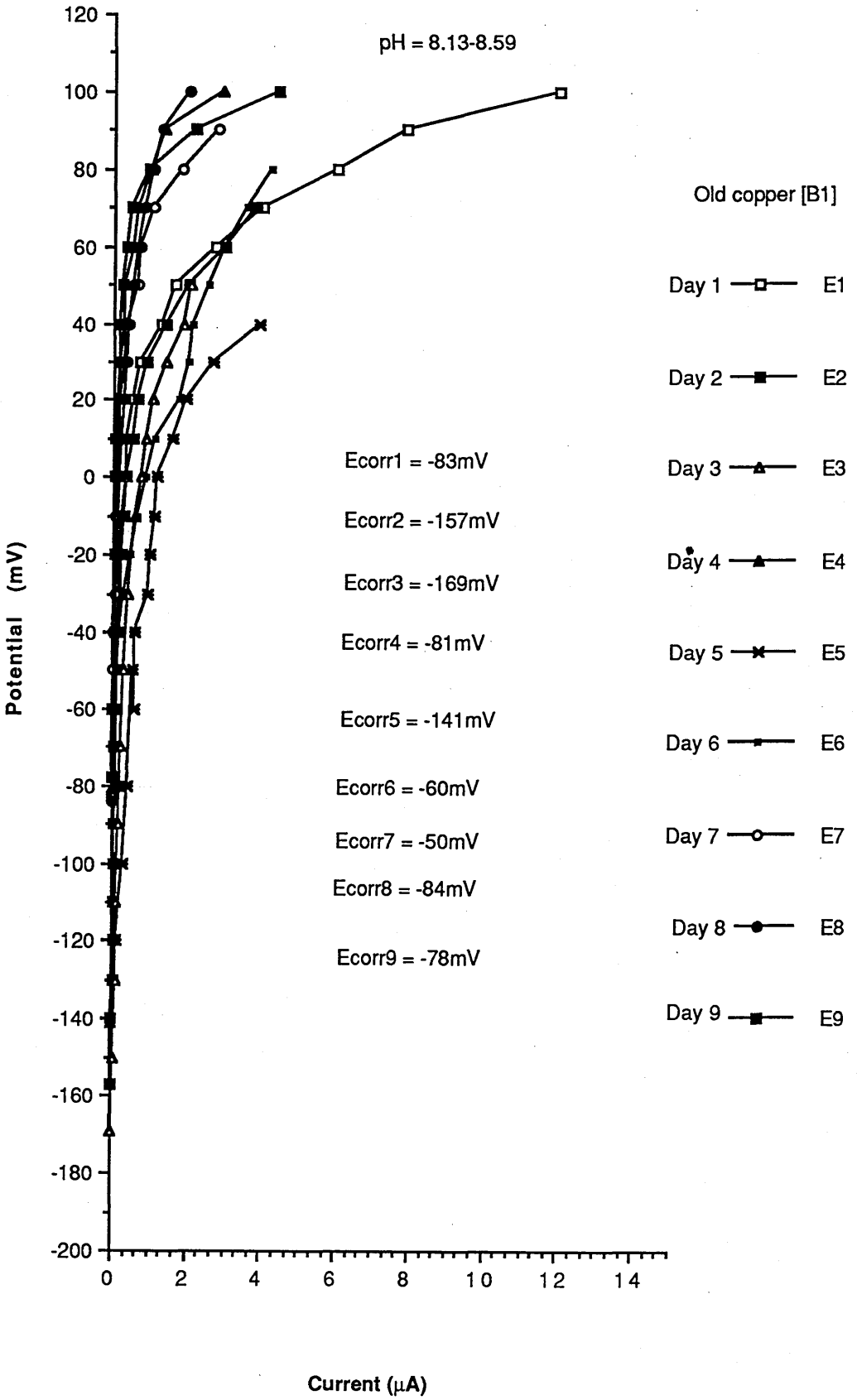
Cold tap water

Anodic polarisation tests of different specimens but immediately after immersion.



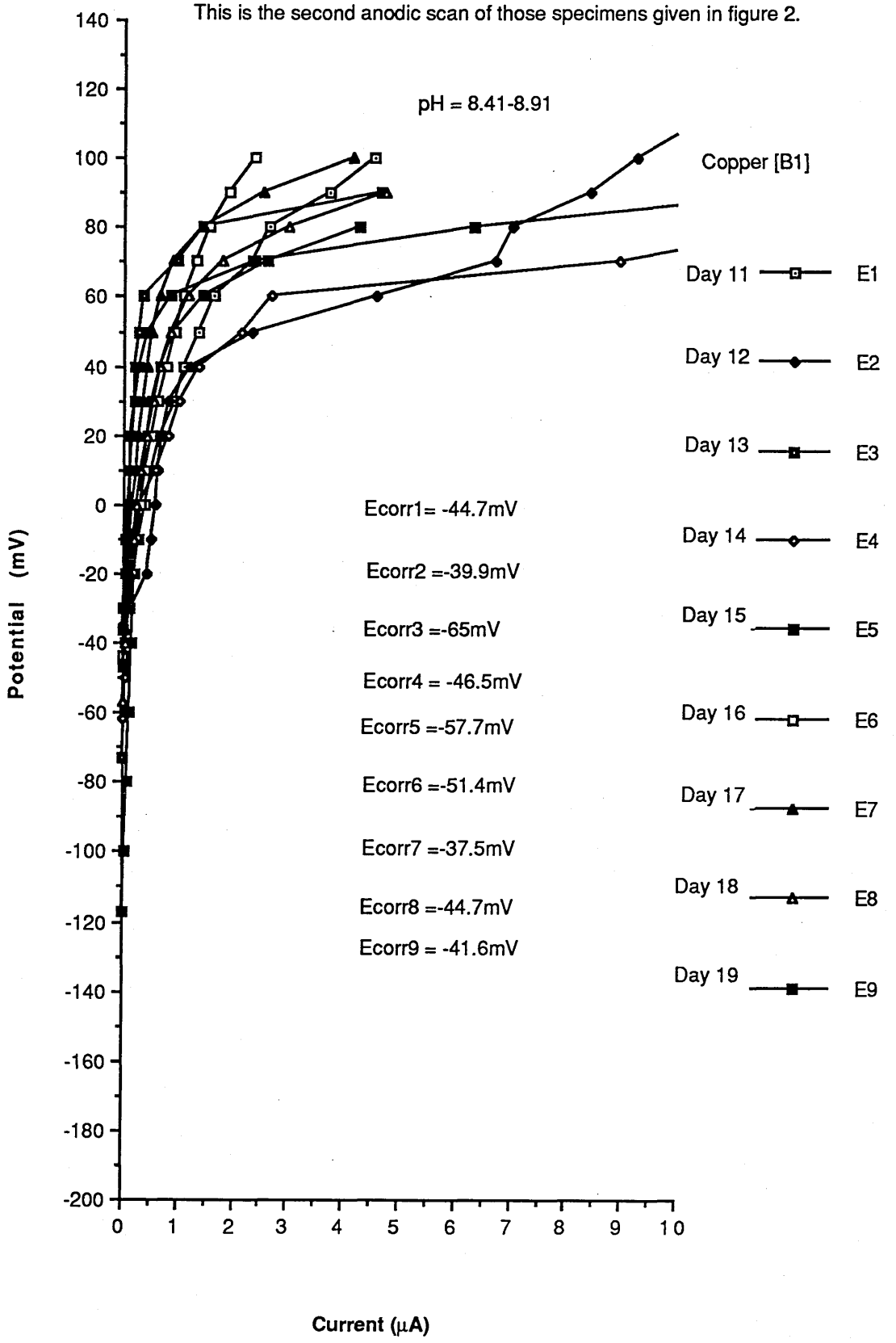
Moving cold water Figure 2

Anodic polarisation experiments on different specimens each exposed for the time indicated.



In each case the specimens were left untouched for 10 days after the first scan as shown in figure 2.

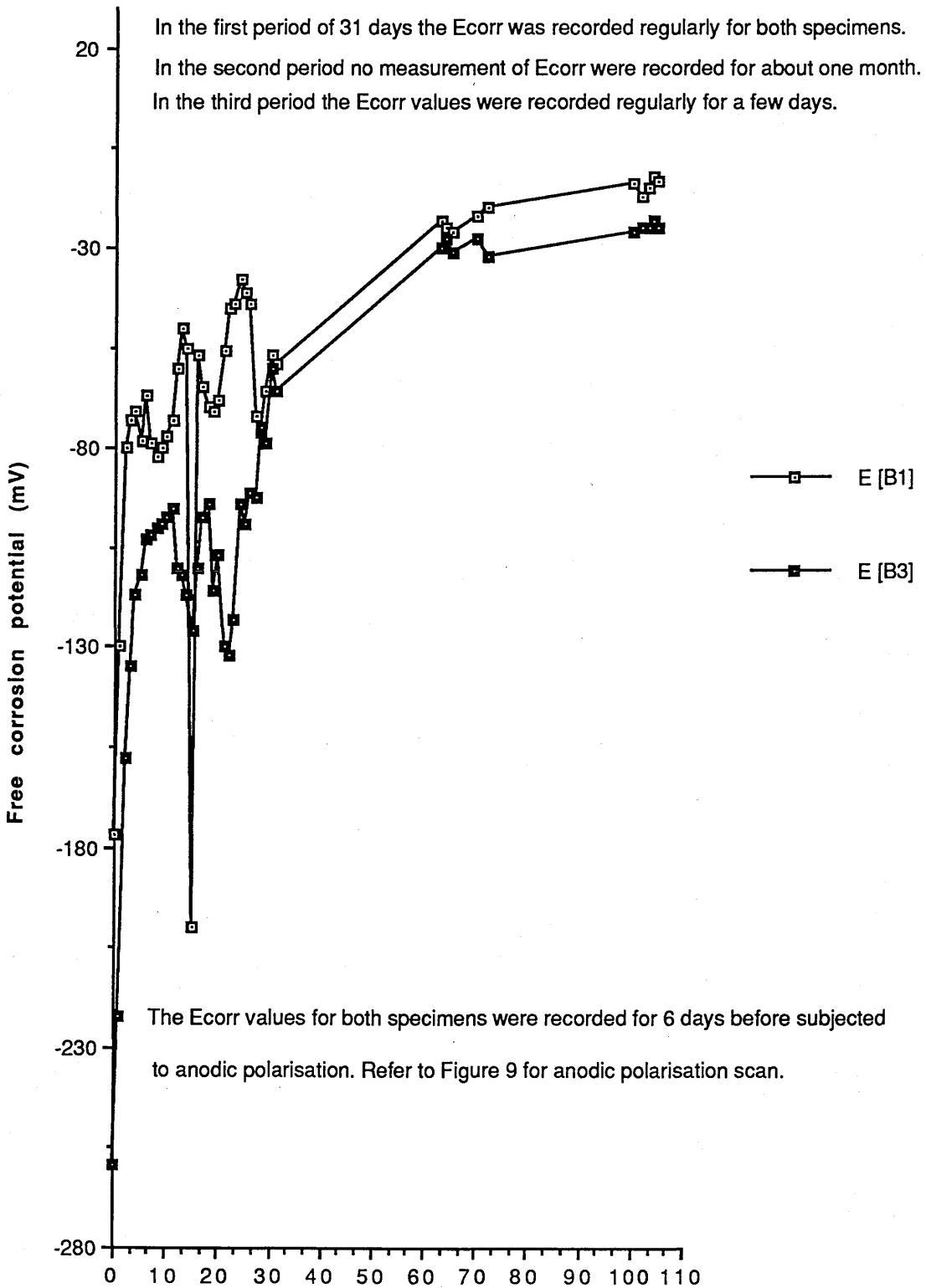
This is the second anodic scan of those specimens given in figure 2.



Moving cold water Figure 4

Trend in Free corrosion potential of both grades of copper specimens with the length of time.

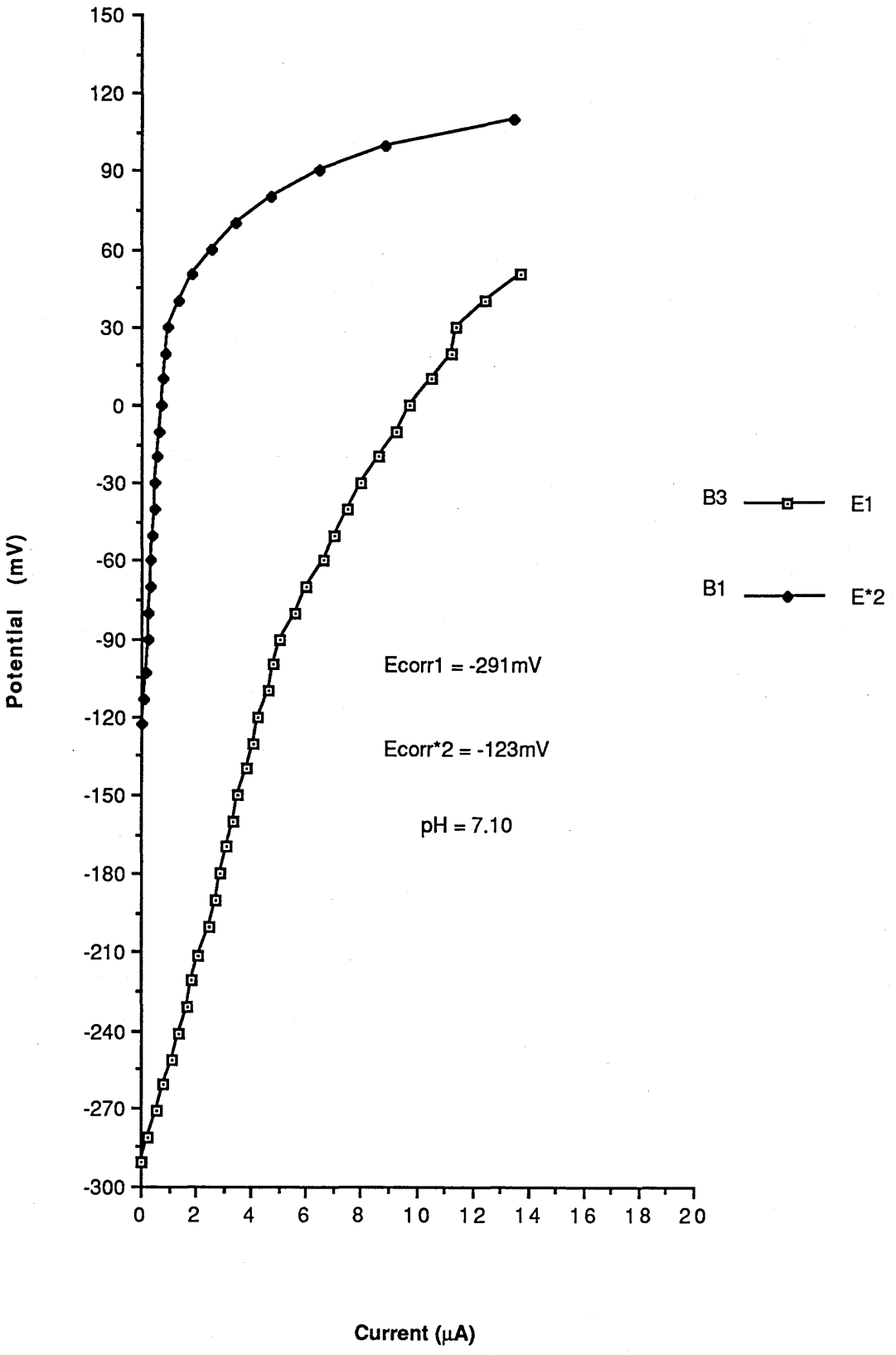
In the first period of 31 days the Ecorr was recorded regularly for both specimens.
In the second period no measurement of Ecorr were recorded for about one month.
In the third period the Ecorr values were recorded regularly for a few days.



The Ecorr values for both specimens were recorded for 6 days before subjected to anodic polarisation. Refer to Figure 9 for anodic polarisation scan.

Moving cold water Figure 5

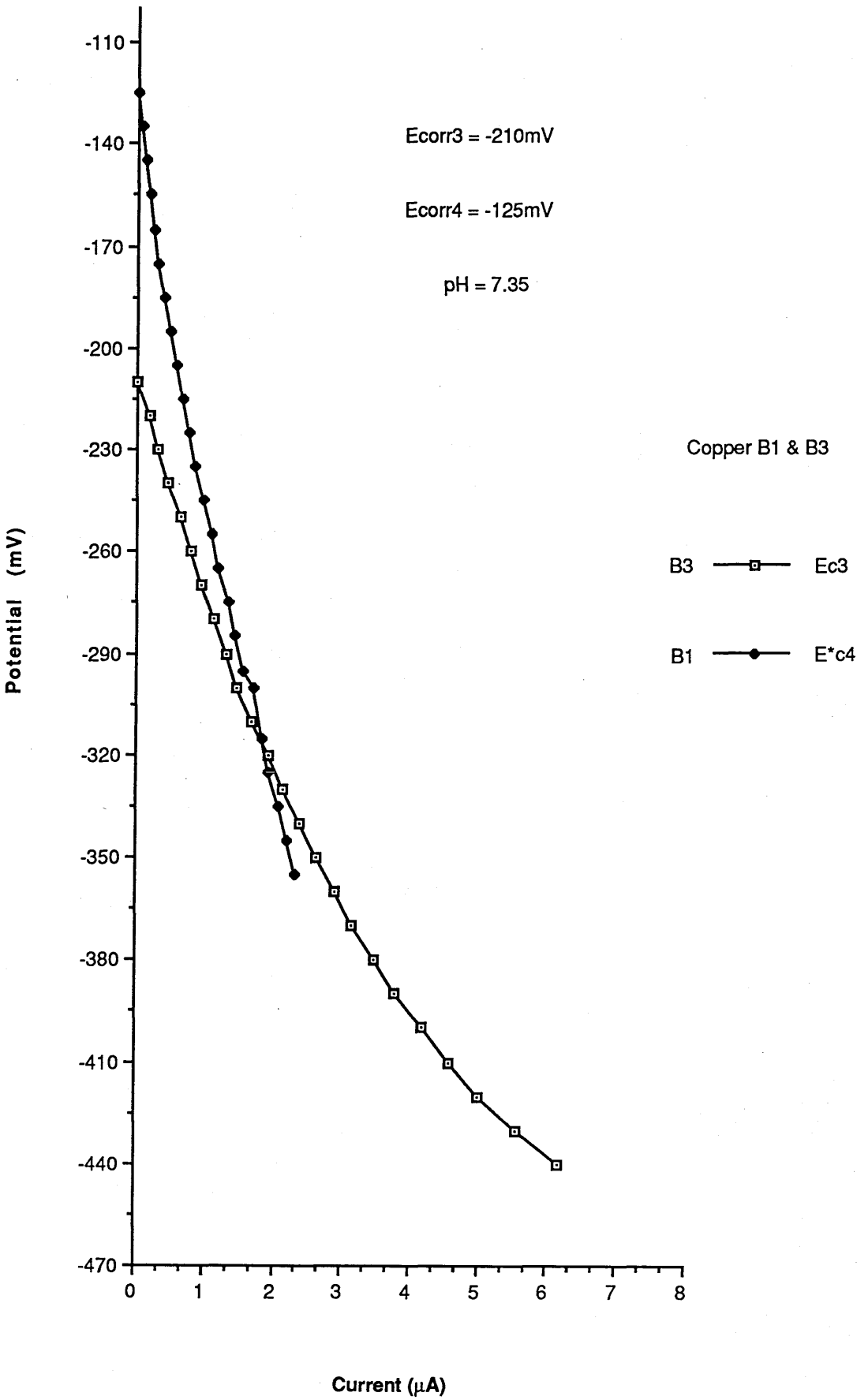
Anodic scan after one day of immersion in cold water.



Moving cold water

Figure 6

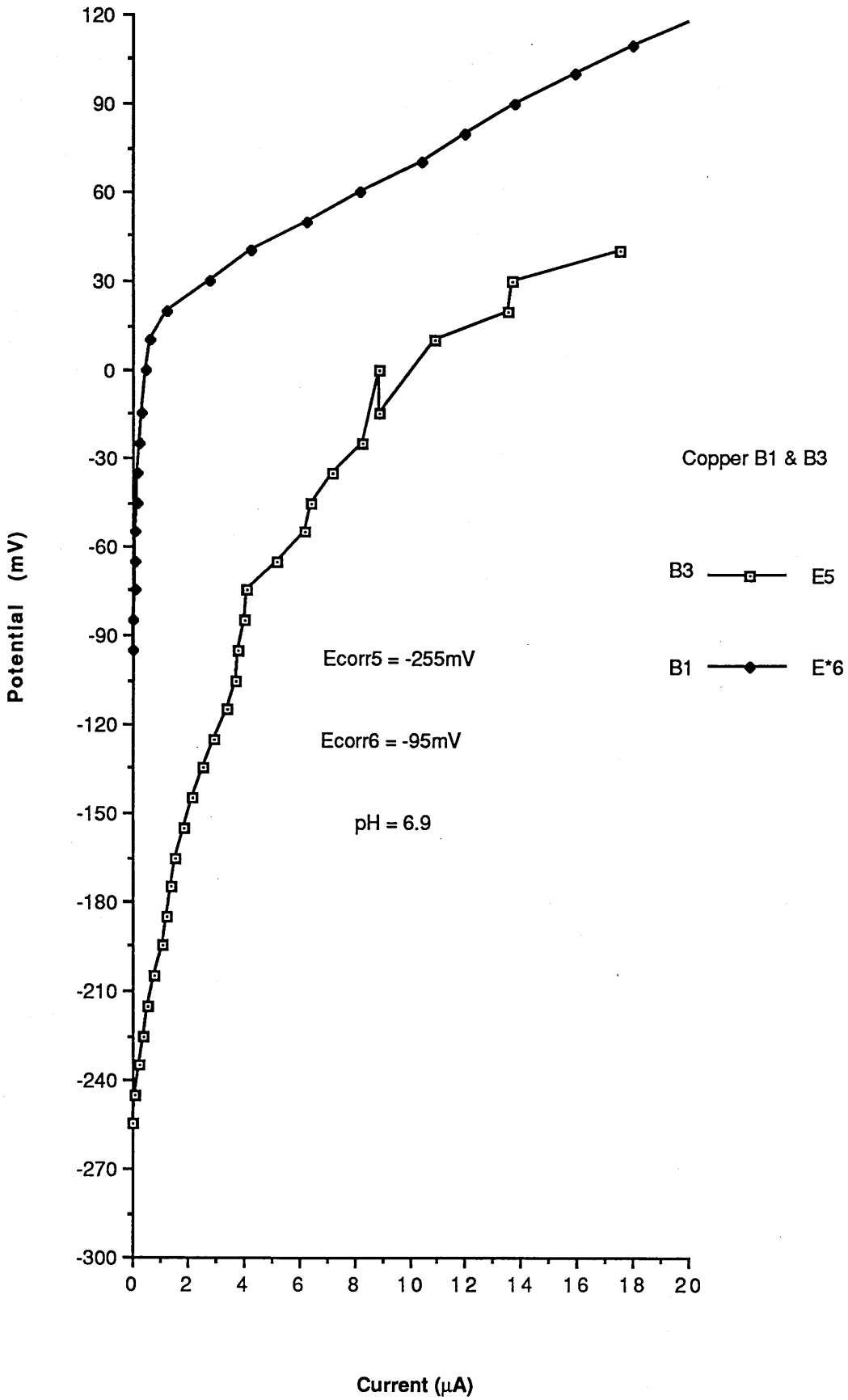
Cathodic scan after one day of immersion.



Moving cold water

Figure 7

Anodic scan after six days of immersion.



Moving cold water

Figure 8

Cathodic scan after six days of immersion.

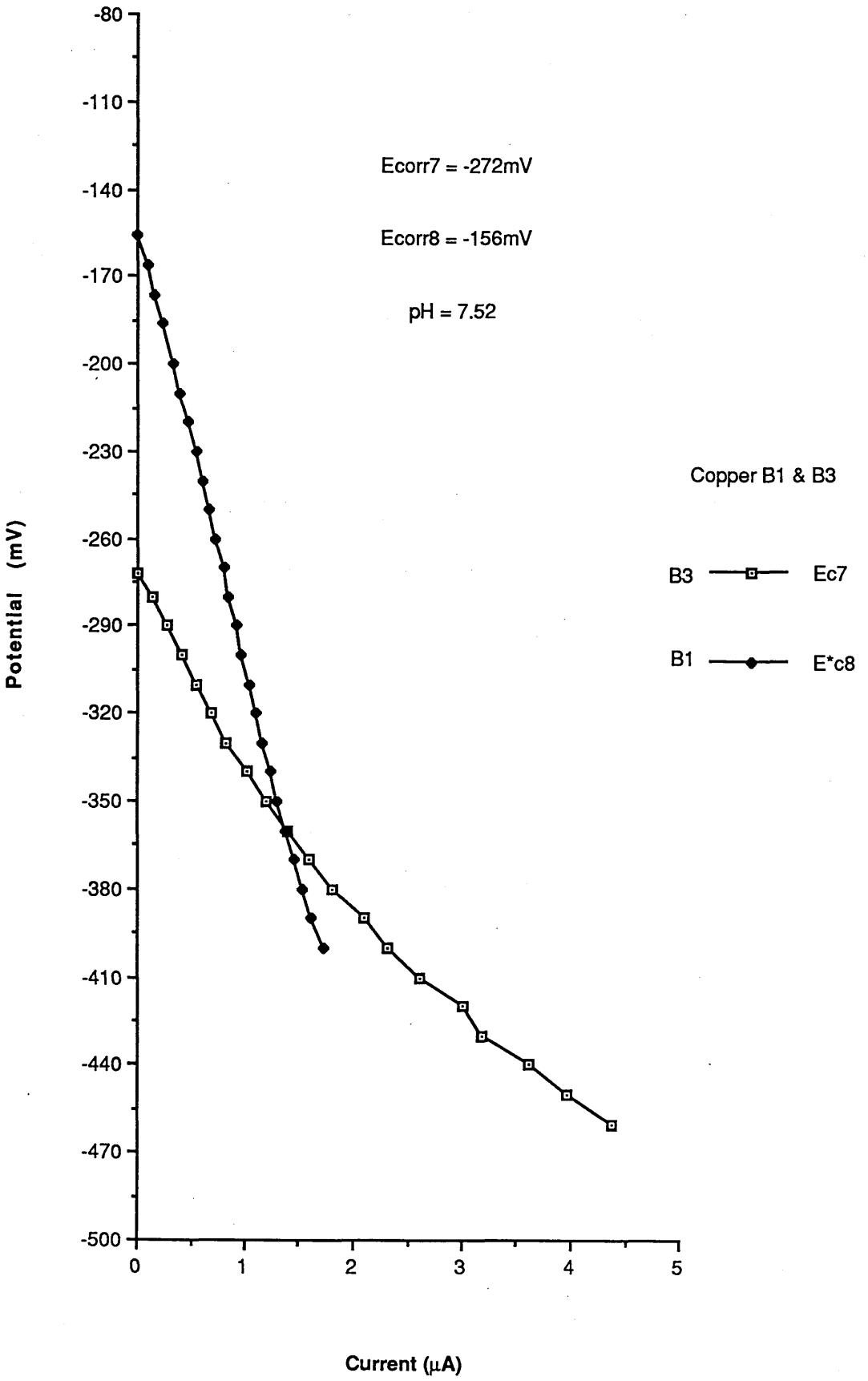
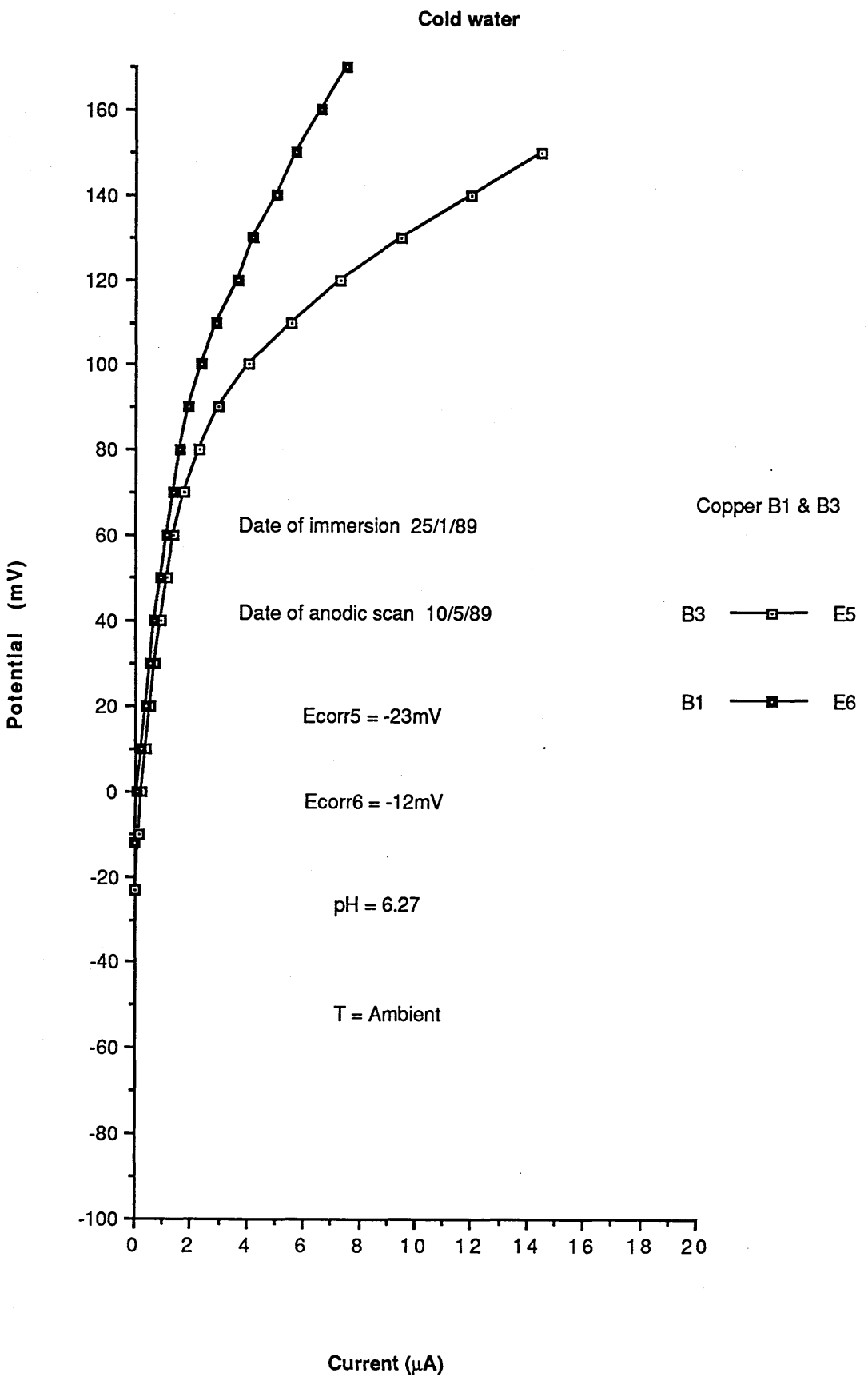
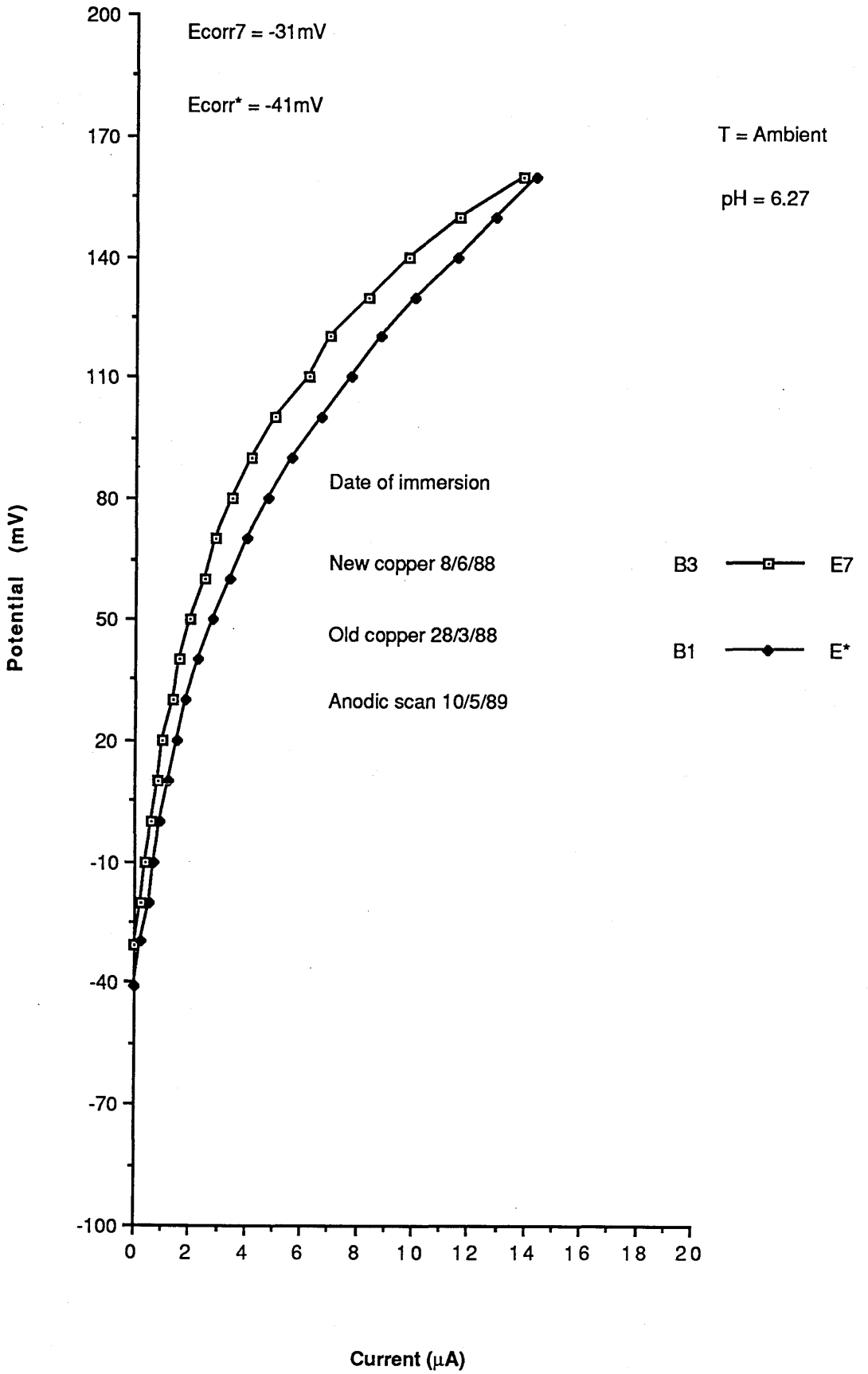


Figure 9


Moving cold water
Cold water
Potential (mV)
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
0
2
4
6
8
10
12
14
16
18
20
Current (μA)
Date of immersion 25/1/89
Date of anodic scan 10/5/89
Ecorr5 = -23mV
Ecorr6 = -12mV
pH = 6.27
T = Ambient
Copper B1 & B3
B3 E5
B1 E6

Moving cold water

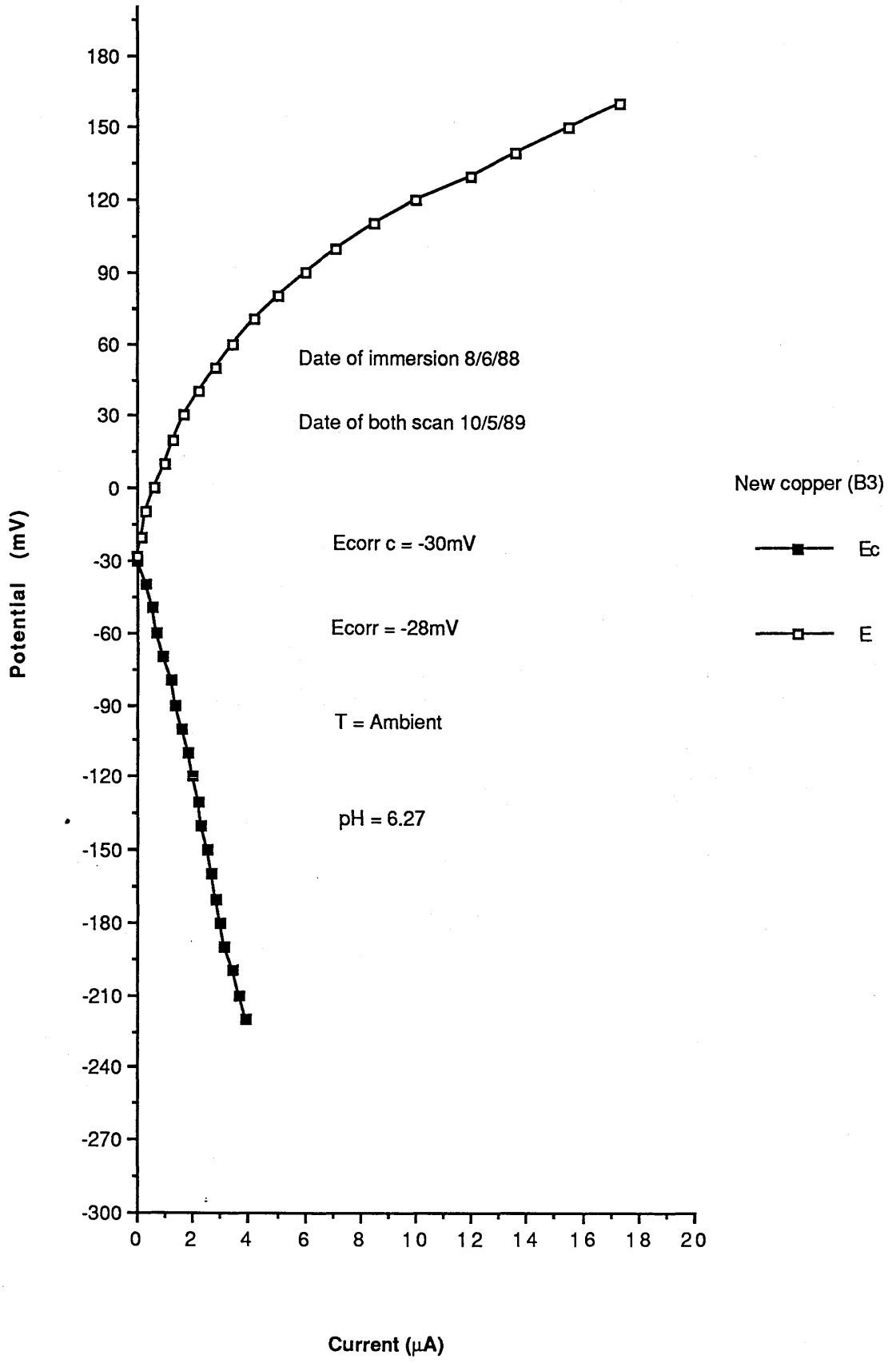
Figure 10



Moving cold water

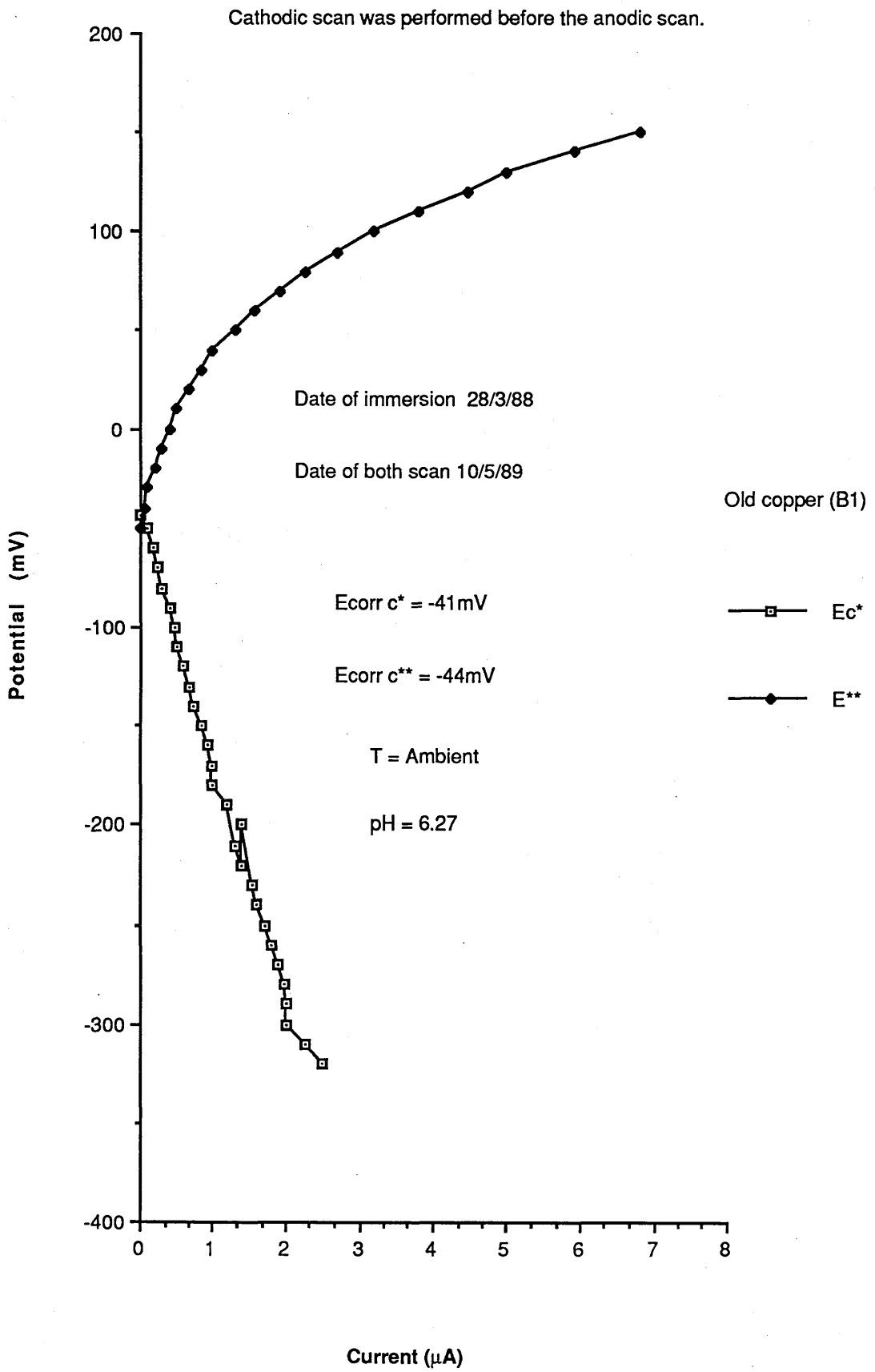
Figure 11

Anodic scan after the cathodic scan.



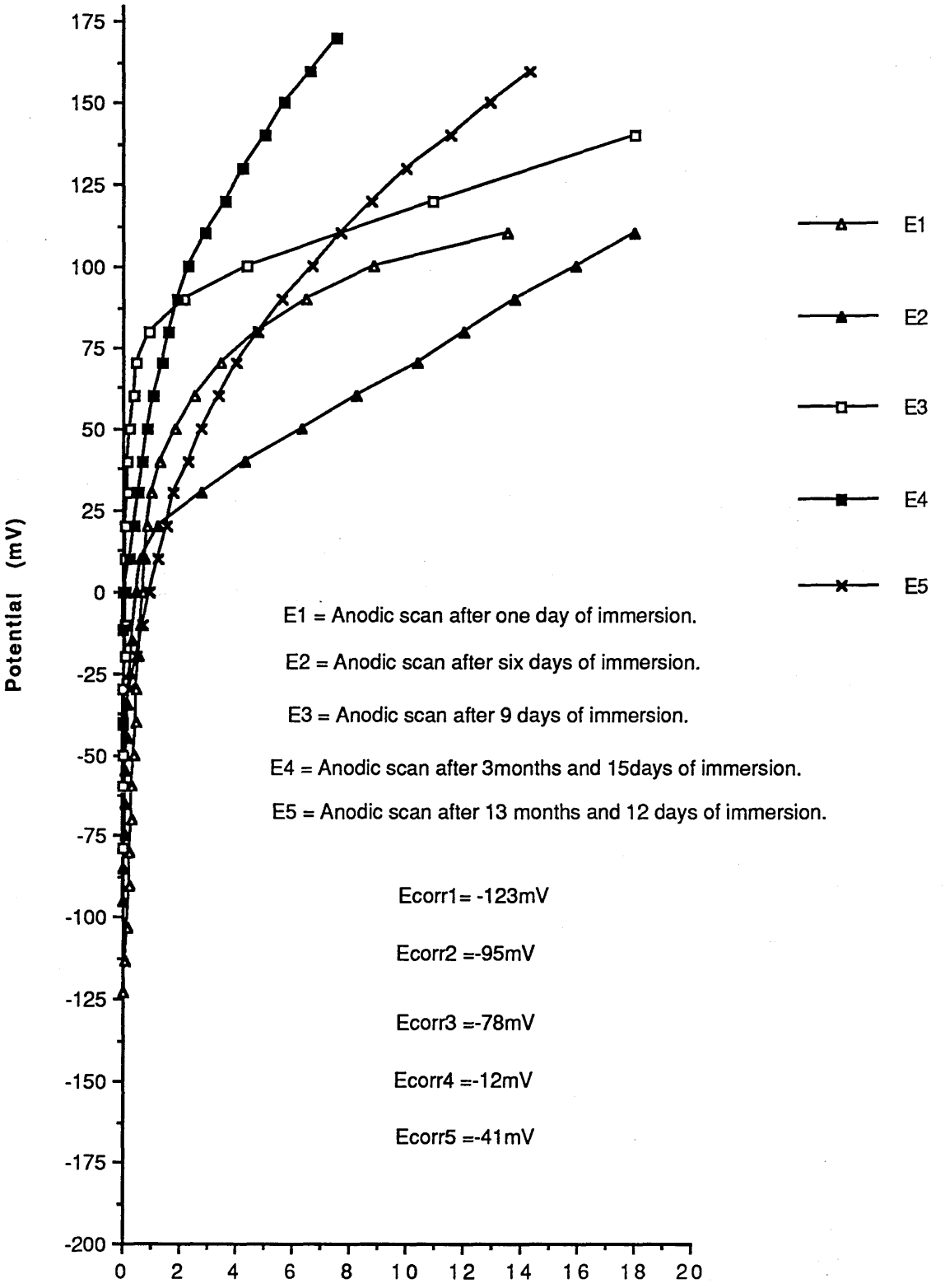
Moving cold water

Figure 12



Moving cold water Figure 13

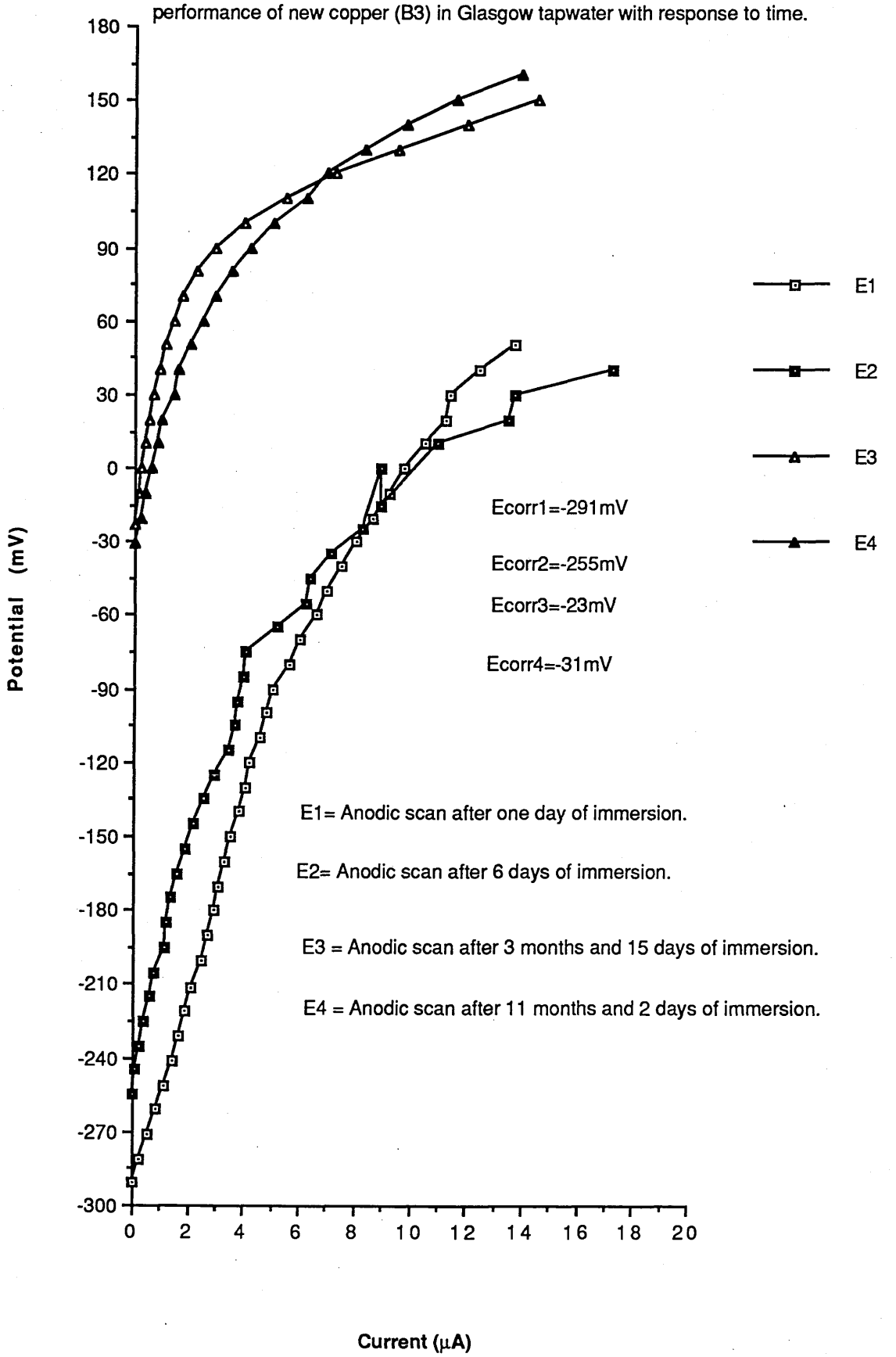
Performance of old copper specimens (B1) with respect to time.



Moving cold water

Figure 14

performance of new copper (B3) in Glasgow tapwater with response to time.

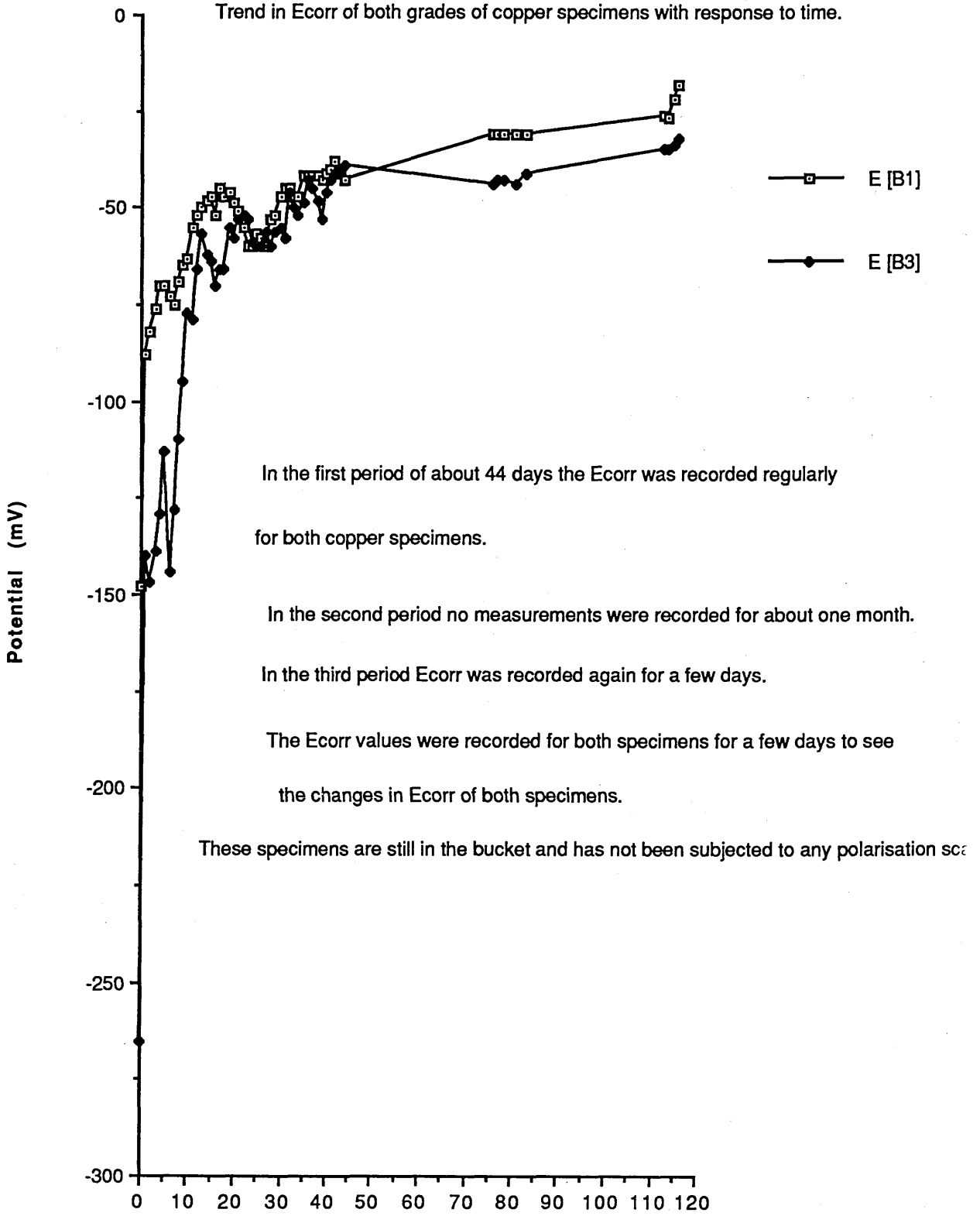


Moving cold water

Figure 15

(Dark condition)

Trend in Ecorr of both grades of copper specimens with response to time.



In the first period of about 44 days the Ecorr was recorded regularly for both copper specimens.

In the second period no measurements were recorded for about one month.

In the third period Ecorr was recorded again for a few days.

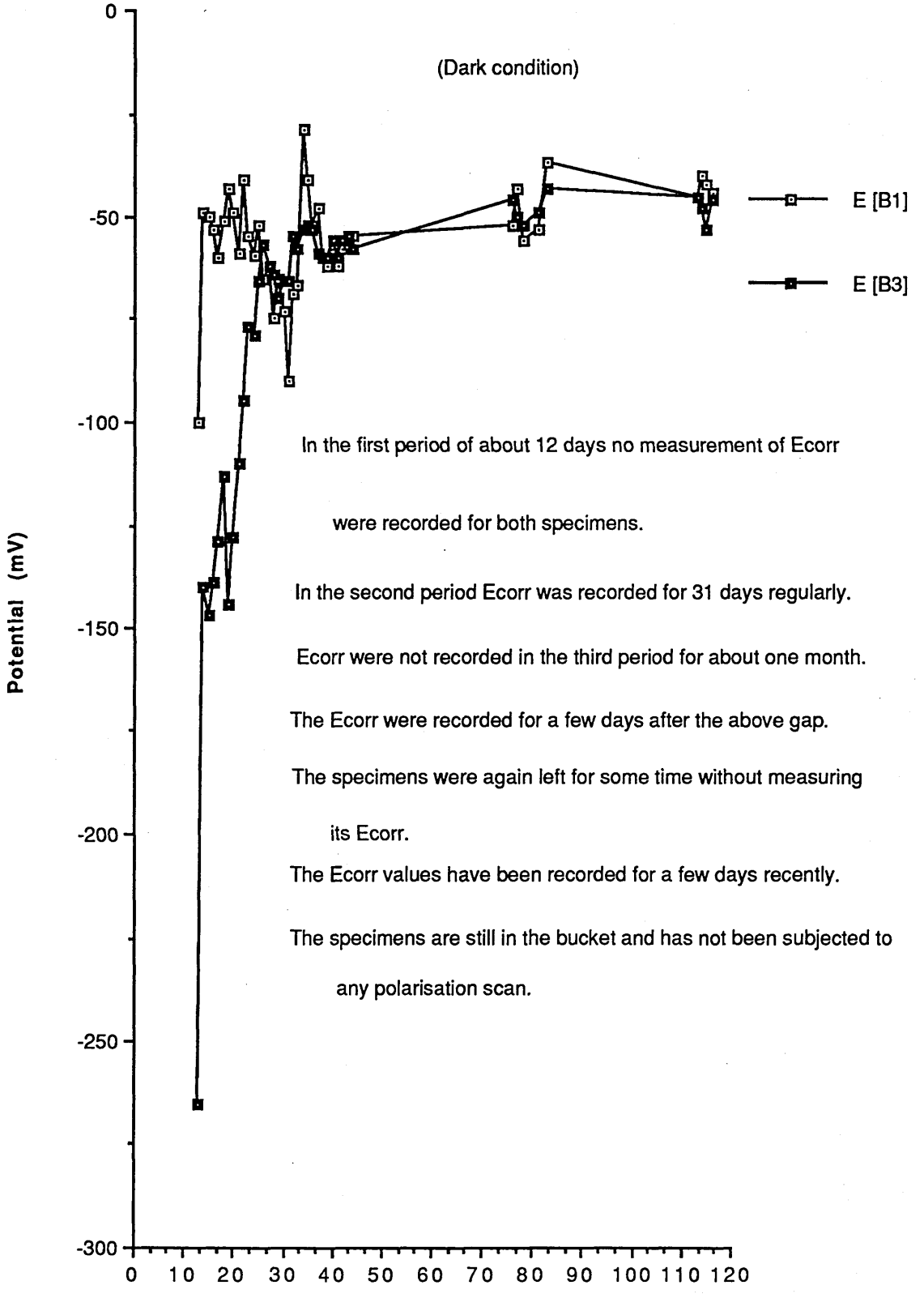
The Ecorr values were recorded for both specimens for a few days to see the changes in Ecorr of both specimens.

These specimens are still in the bucket and has not been subjected to any polarisation sc

Moving cold water

Figure 16

Trend in Ecorr of both grades of copper specimens with the length of time.

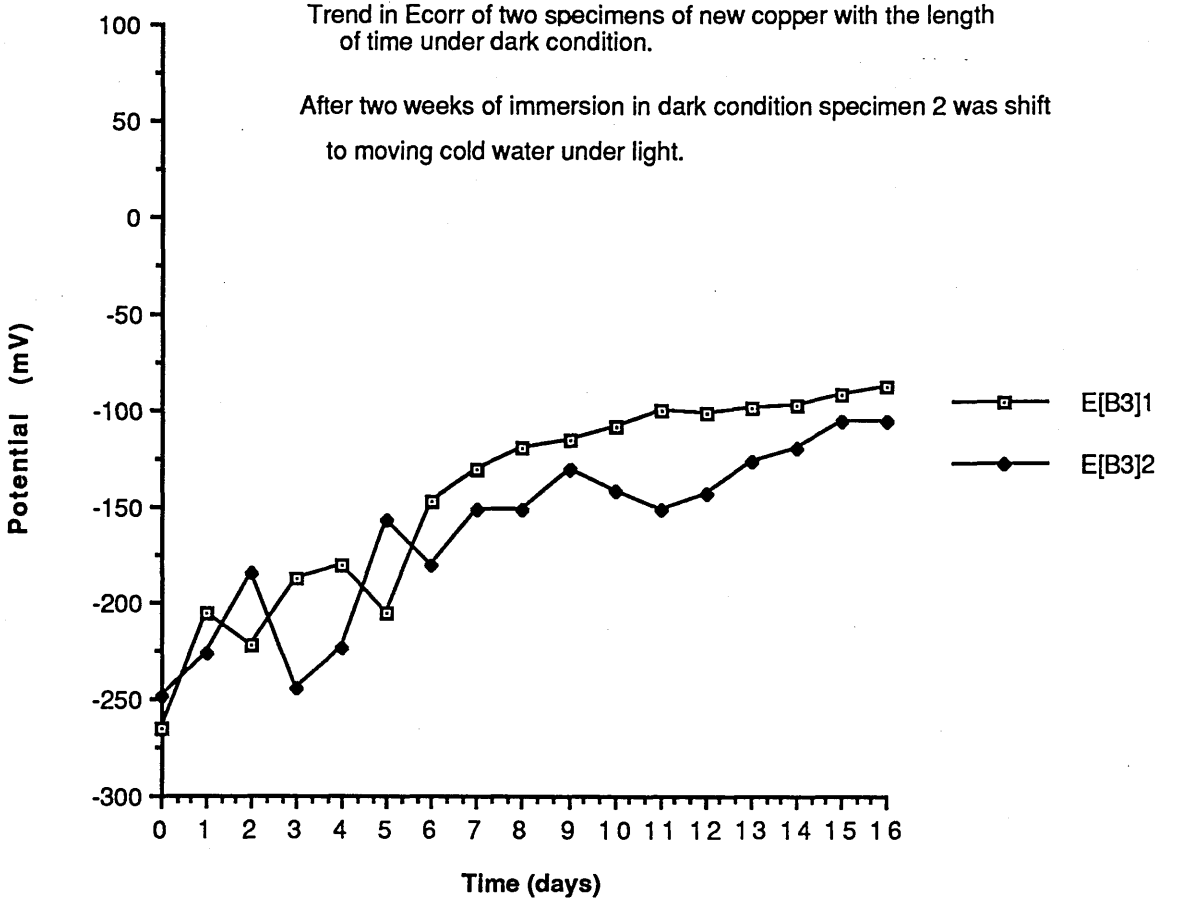


Moving cold water

Figure 17

Trend in Ecorr of two specimens of new copper with the length of time under dark condition.

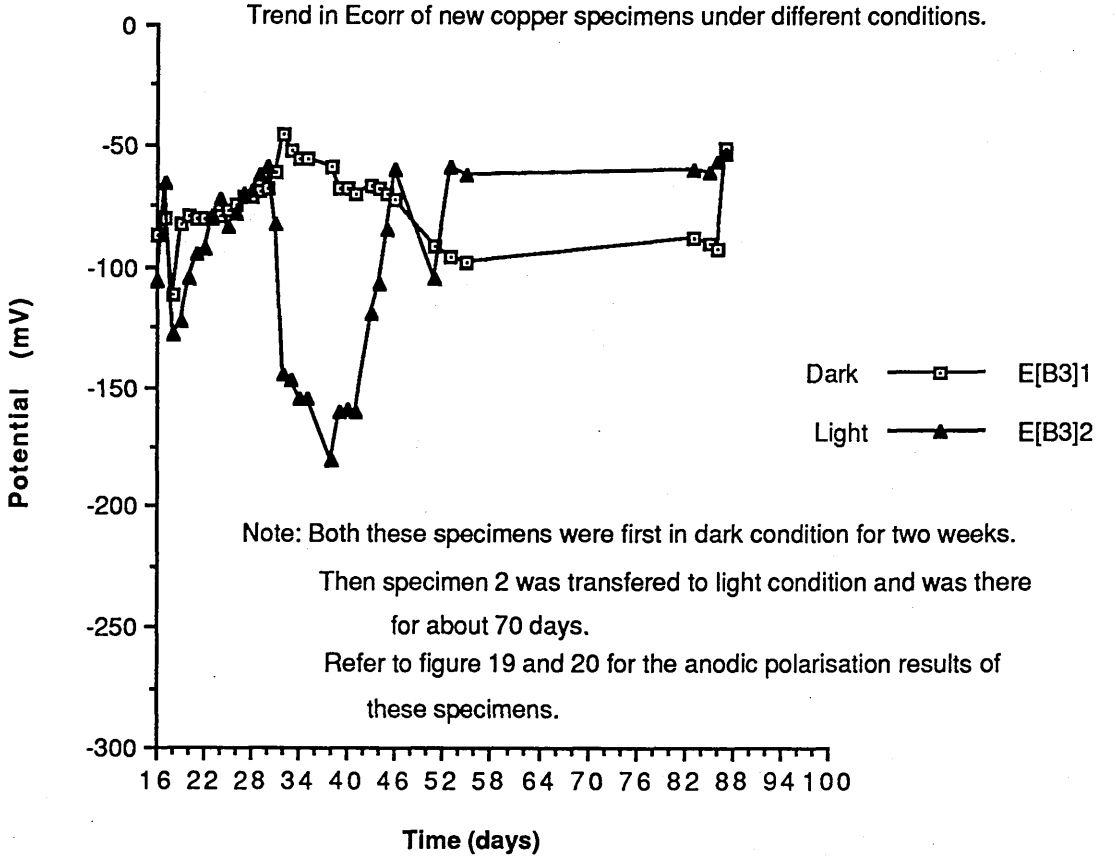
After two weeks of immersion in dark condition specimen 2 was shift to moving cold water under light.



Moving cold water

Figure 17a

Trend in Ecorr of new copper specimens under different conditions.

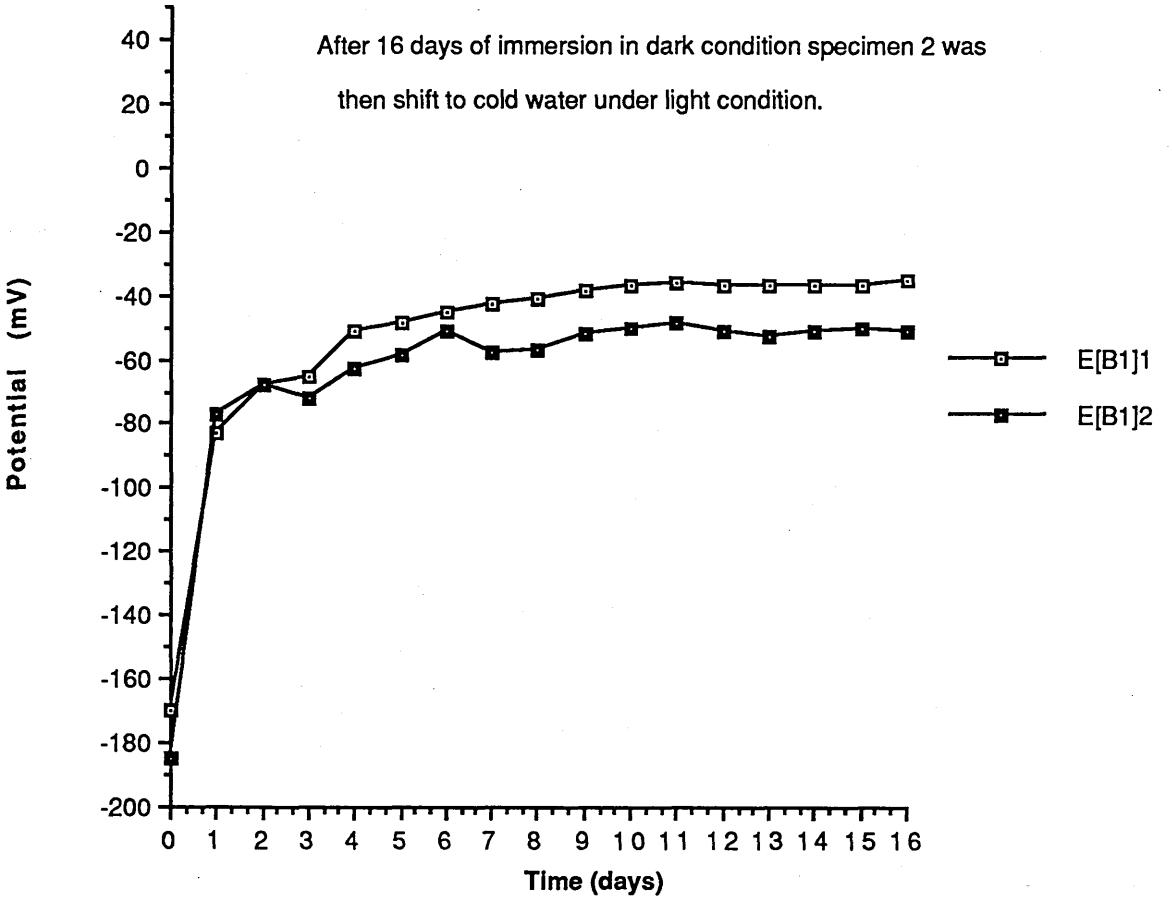


Note: Both these specimens were first in dark condition for two weeks. Then specimen 2 was transfered to light condition and was there for about 70 days.

Refer to figure 19 and 20 for the anodic polarisation results of these specimens.

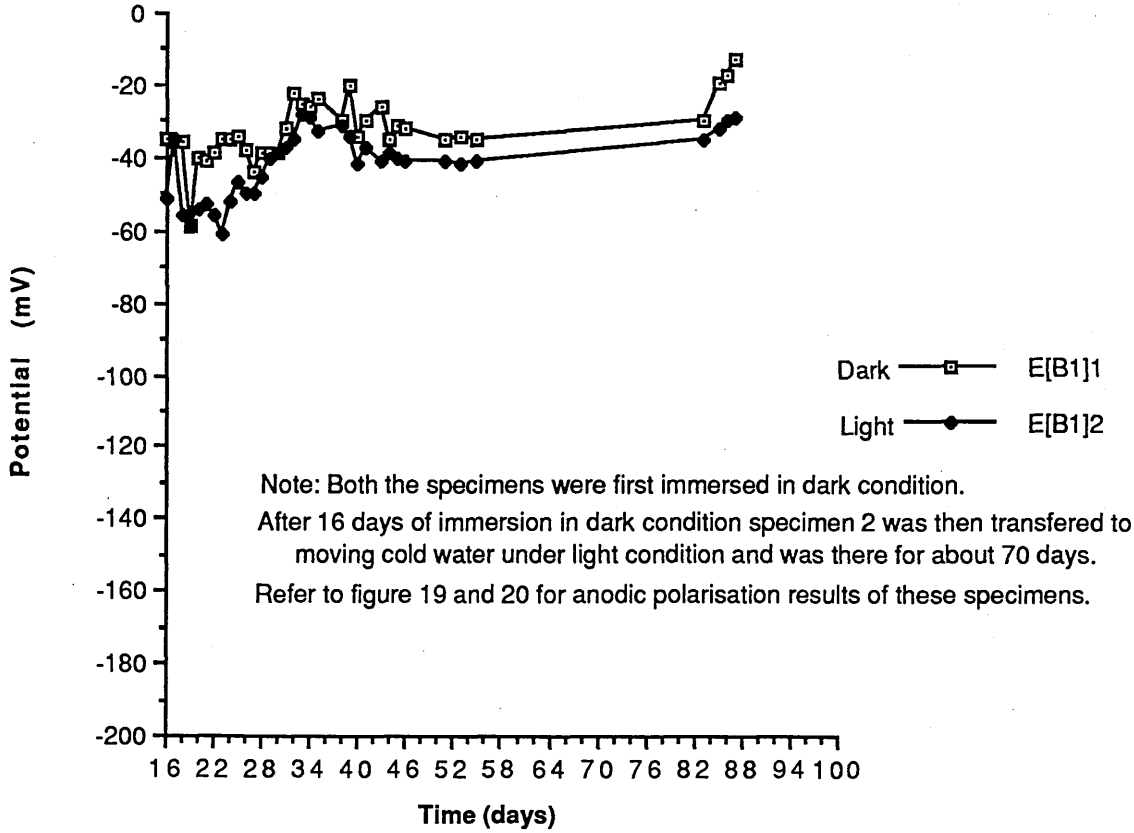
Moving cold water Figure 18

Trend in Ecorr of two old copper specimens with respect to in dark condition.



Moving cold water Figure 18a

Trend in Ecorr old copper specimens under different conditions.



Note: Both the specimens were first immersed in dark condition.
After 16 days of immersion in dark condition specimen 2 was then transfered to moving cold water under light condition and was there for about 70 days.
Refer to figure 19 and 20 for anodic polarisation results of these specimens.

Figure 19

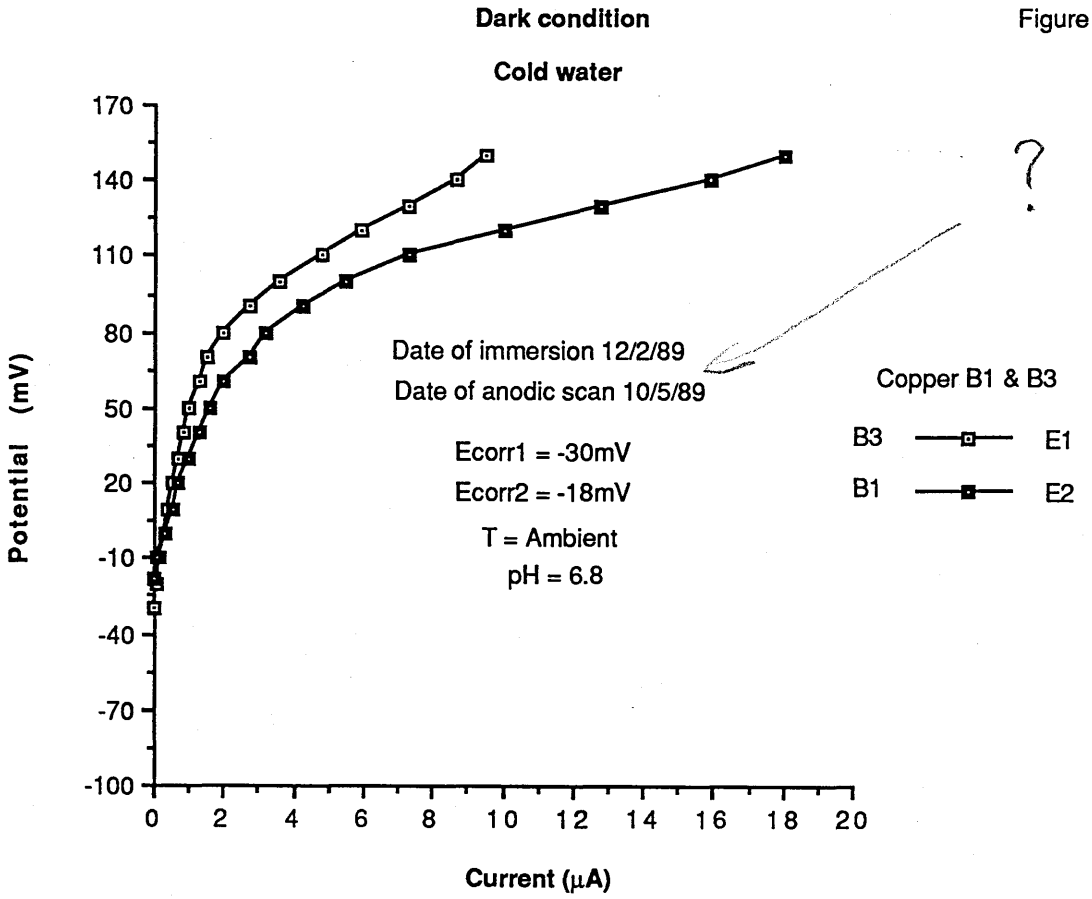
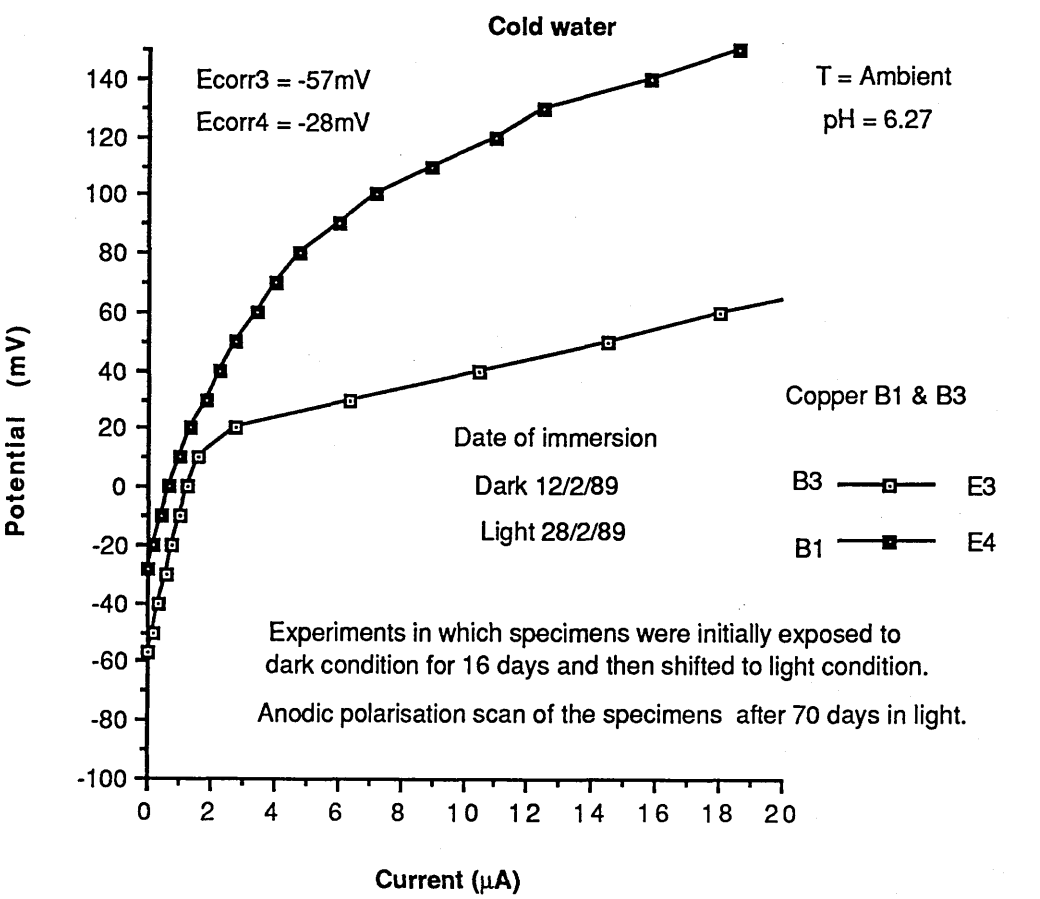
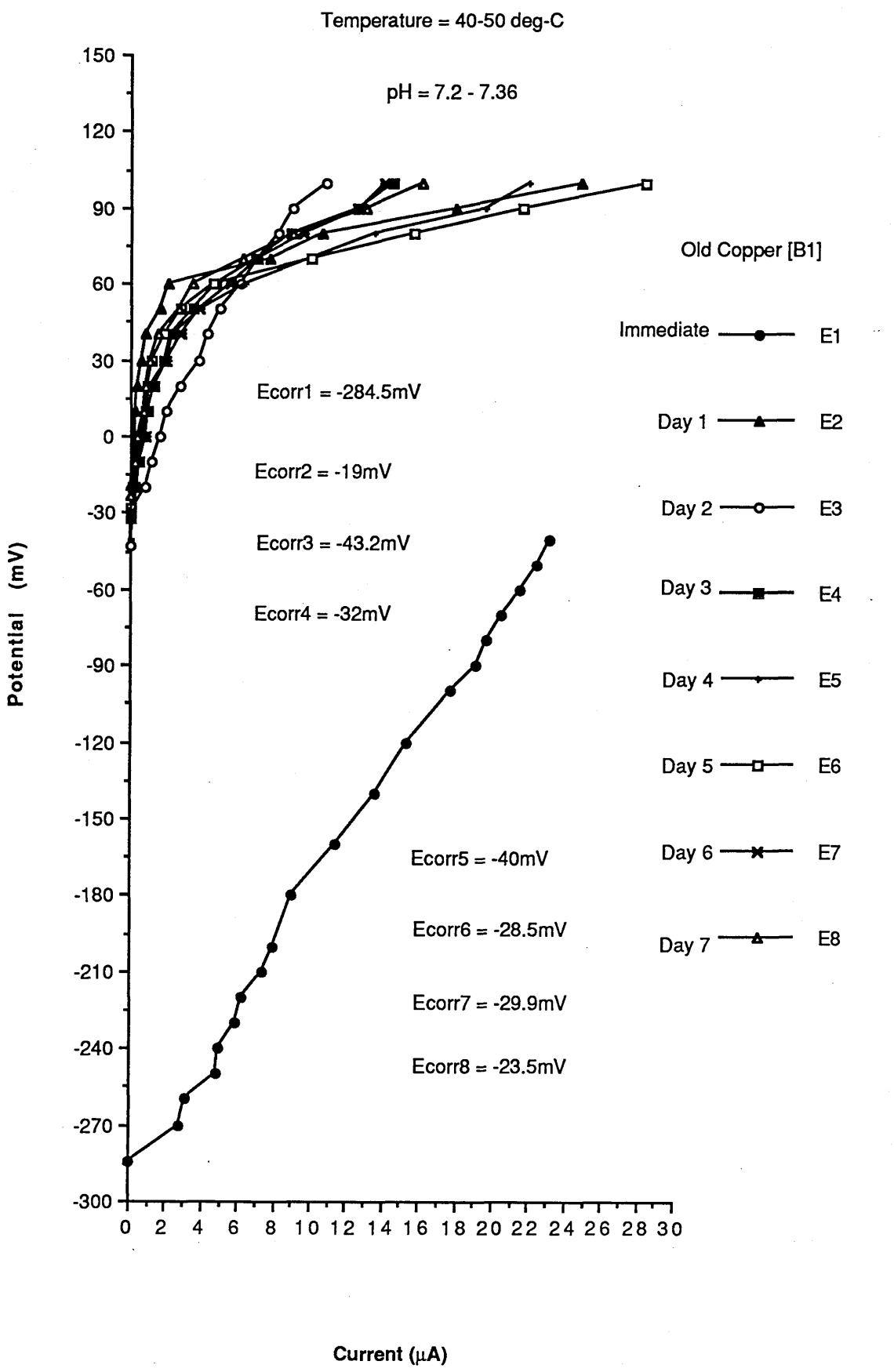


Figure 20

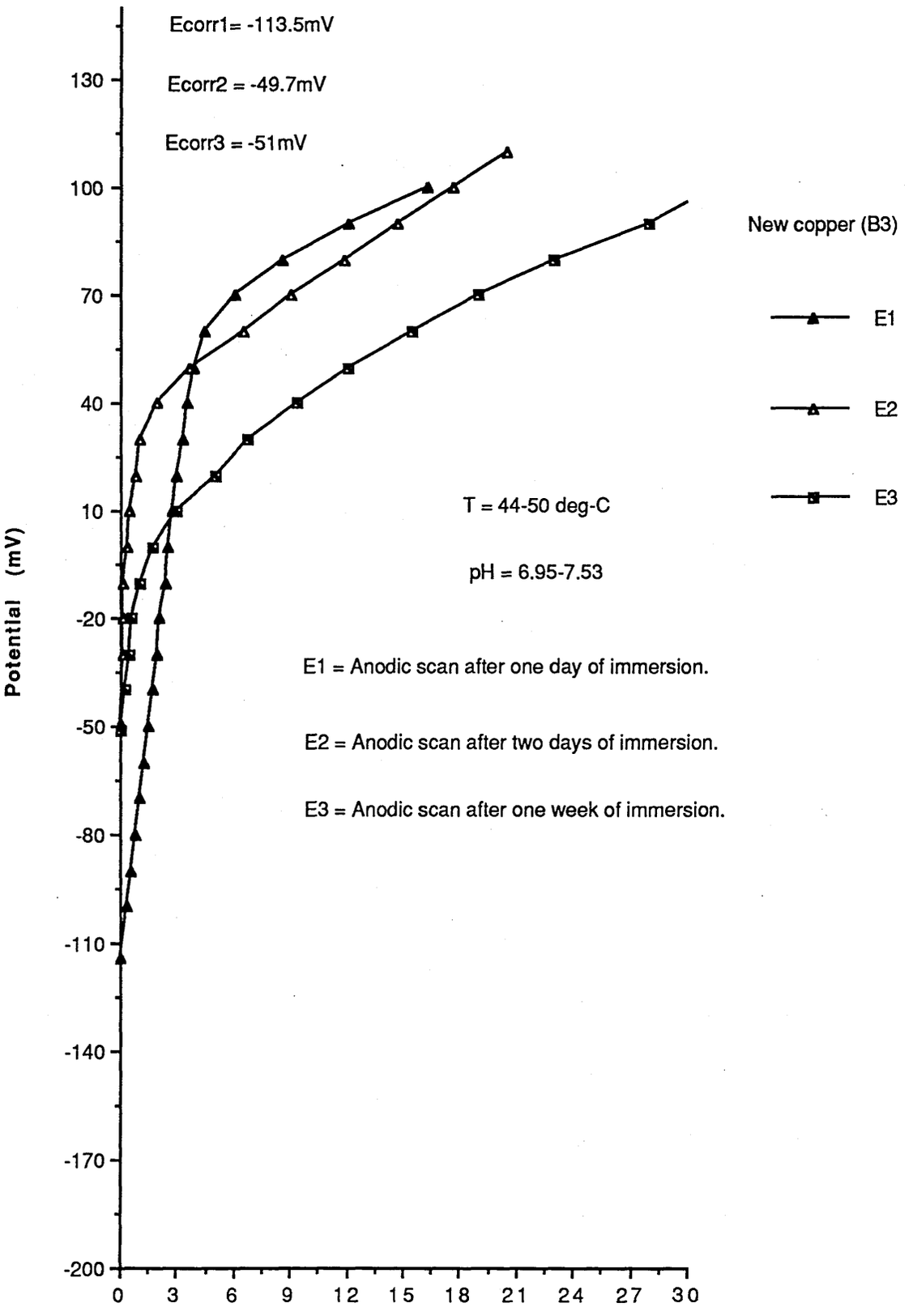


Normal hot water Figure 21



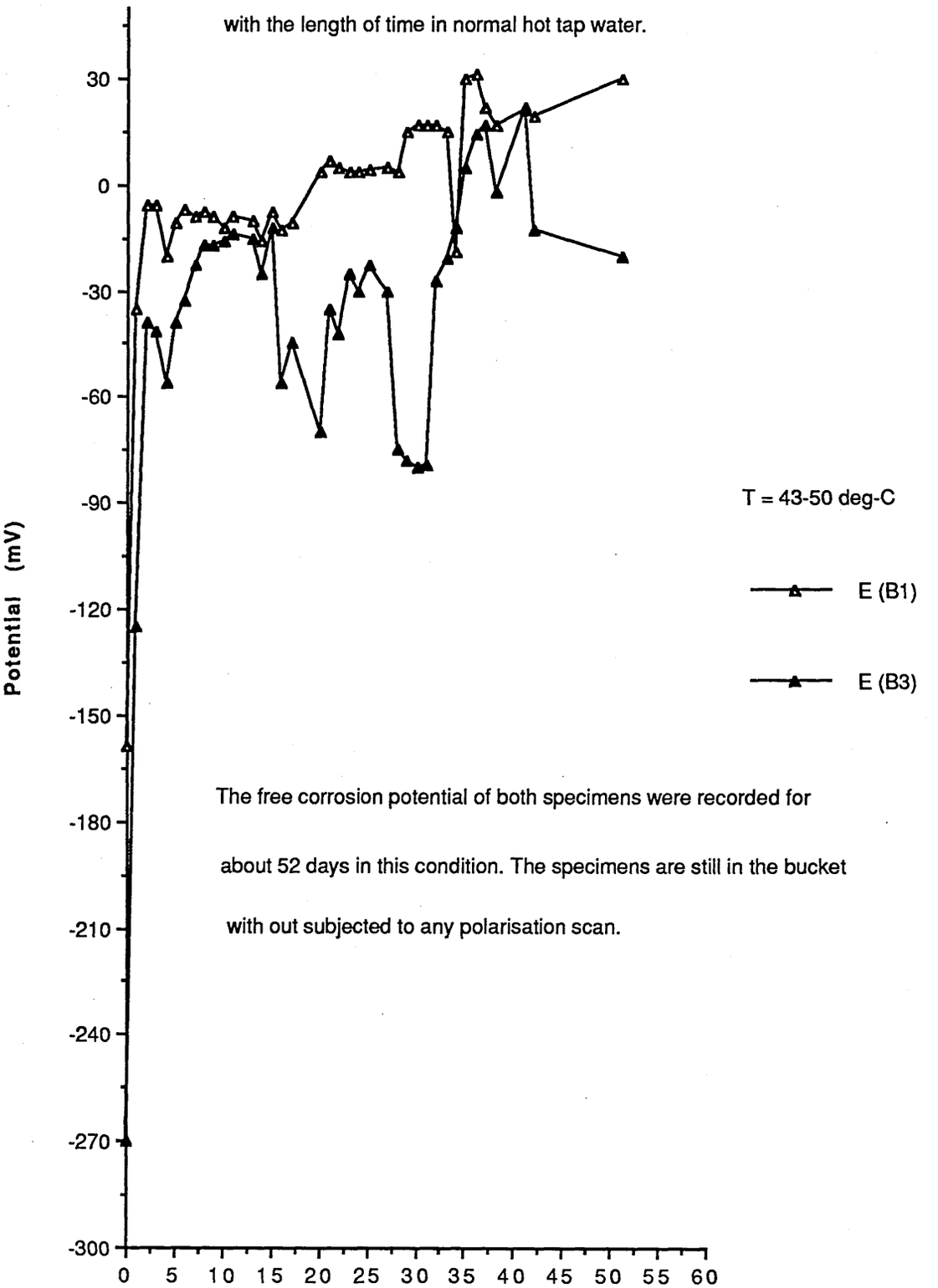
Normal hot water

Figure 22



Normal hot water Figure 23

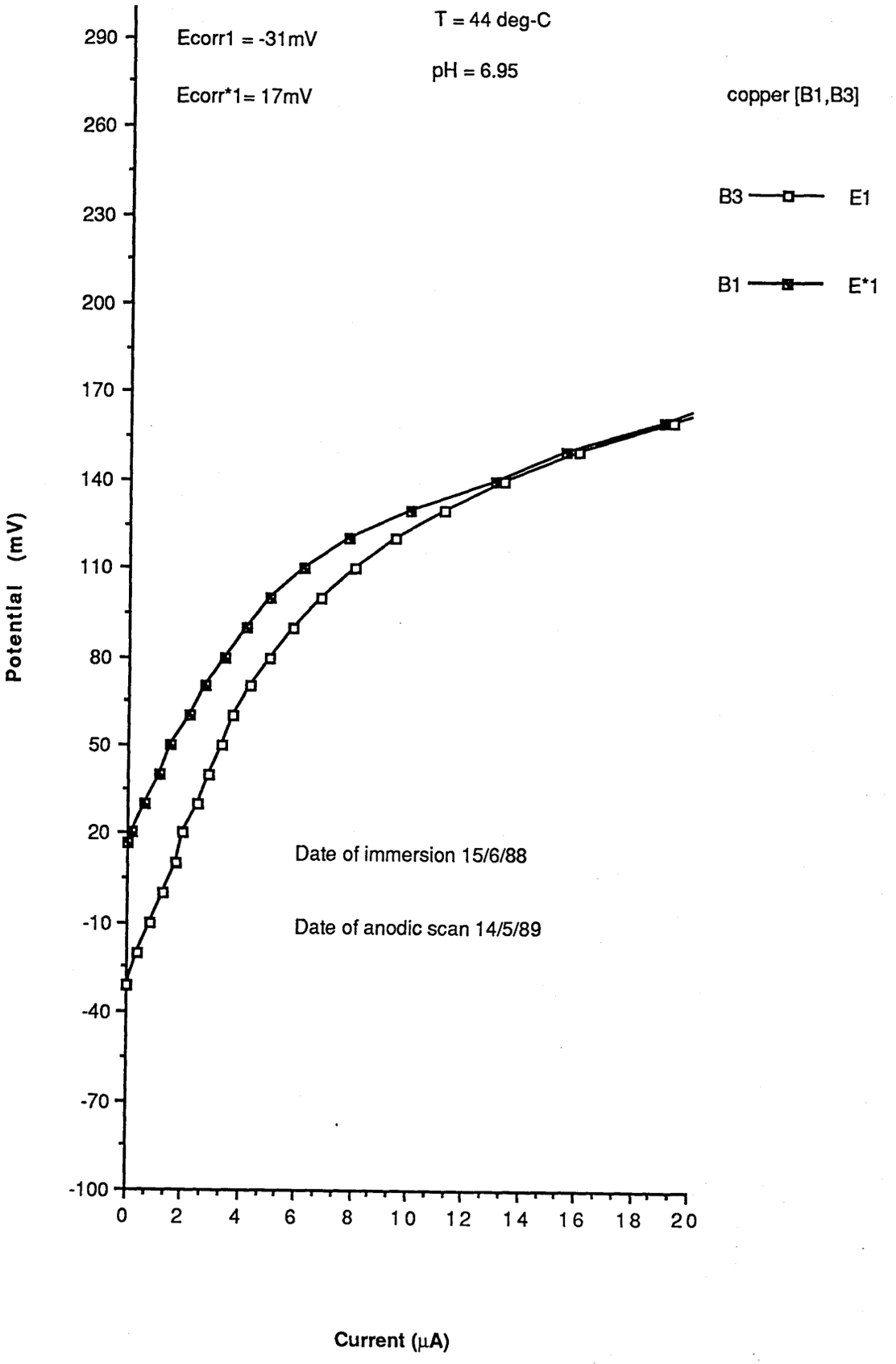
Trend in free corrosion potential of both grades of copper specimens with the length of time in normal hot tap water.



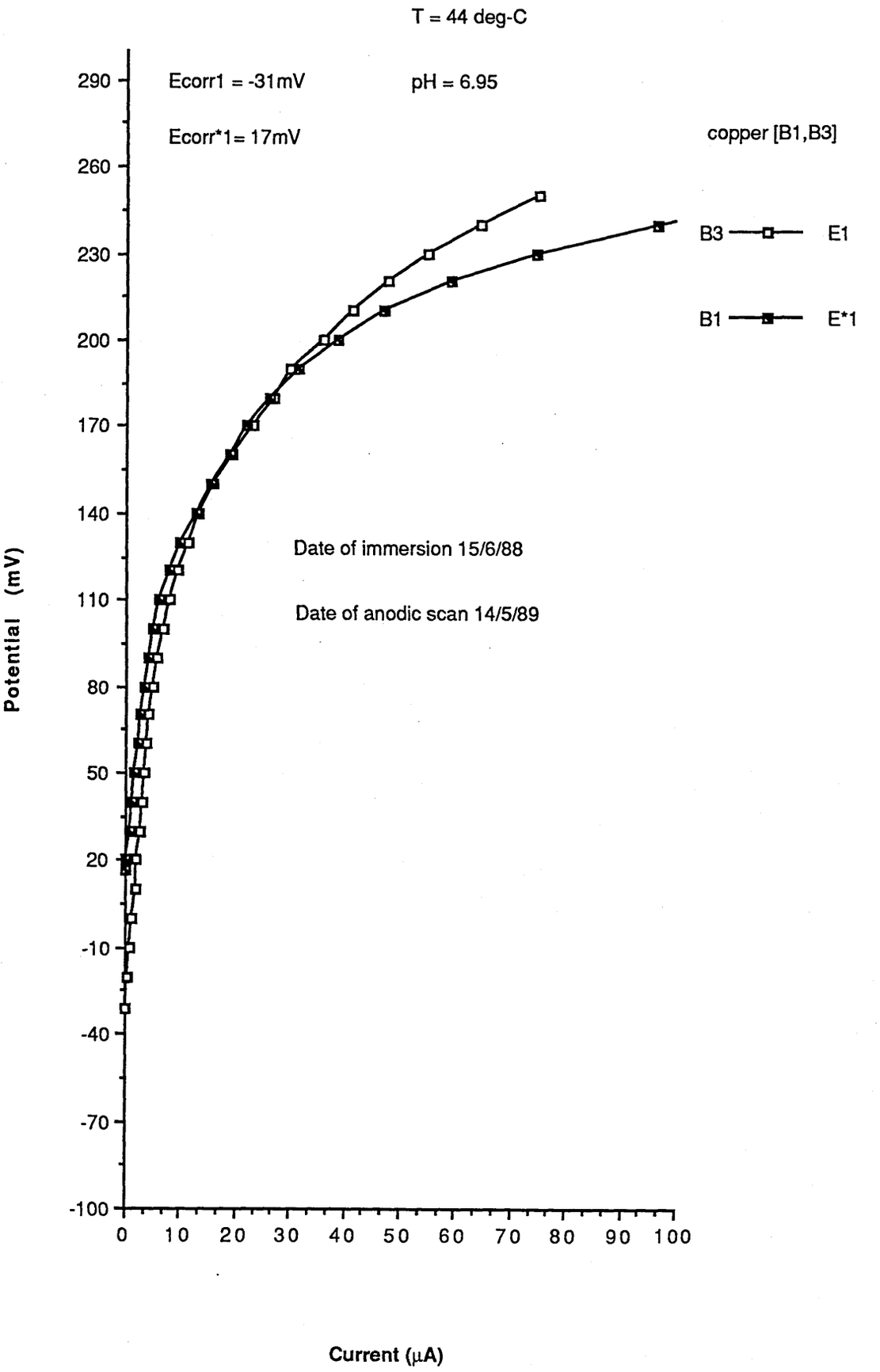
The free corrosion potential of both specimens were recorded for about 52 days in this condition. The specimens are still in the bucket with out subjected to any polarisation scan.

Normal hot water

Figure 24

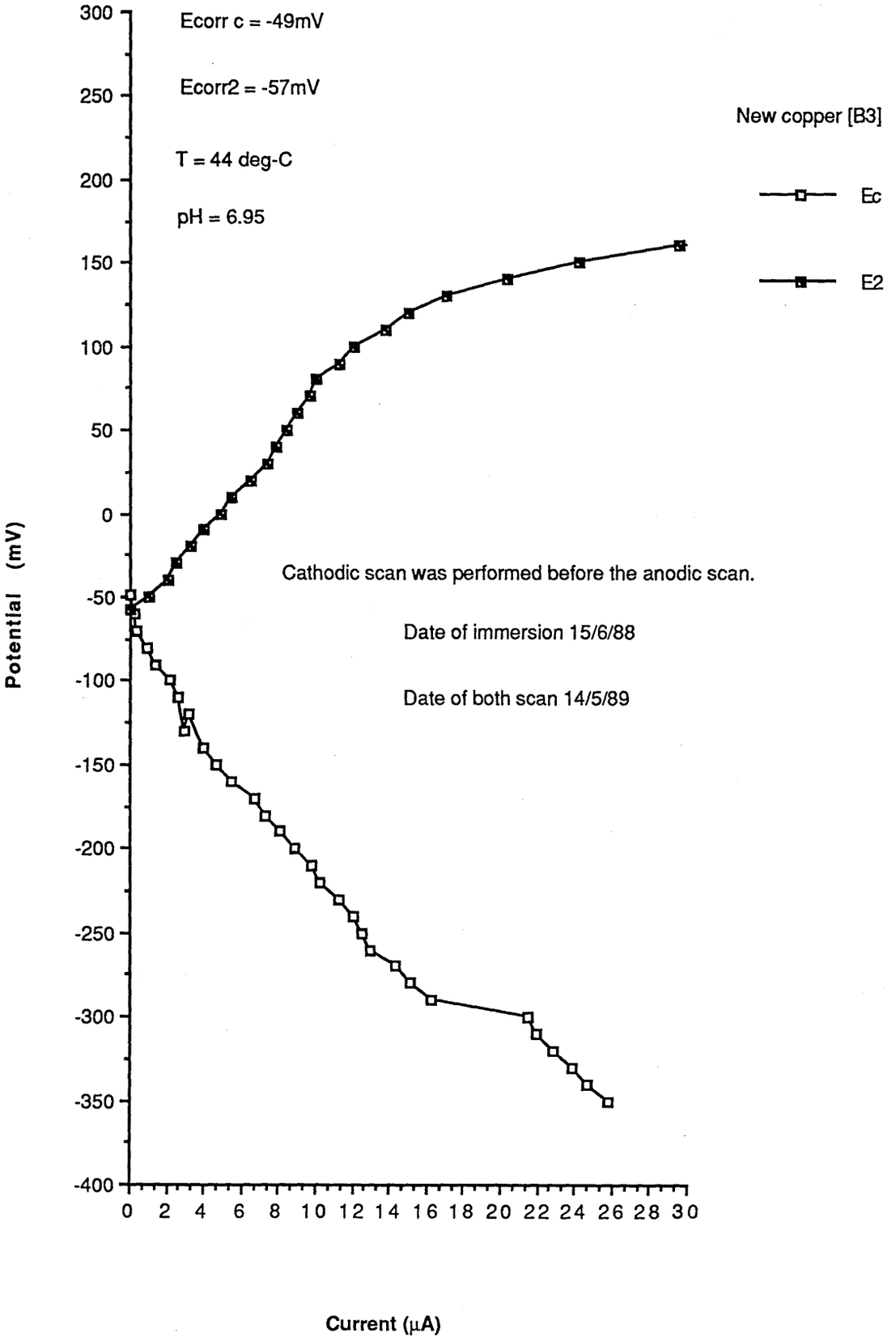


Normal hot water Figure 24A



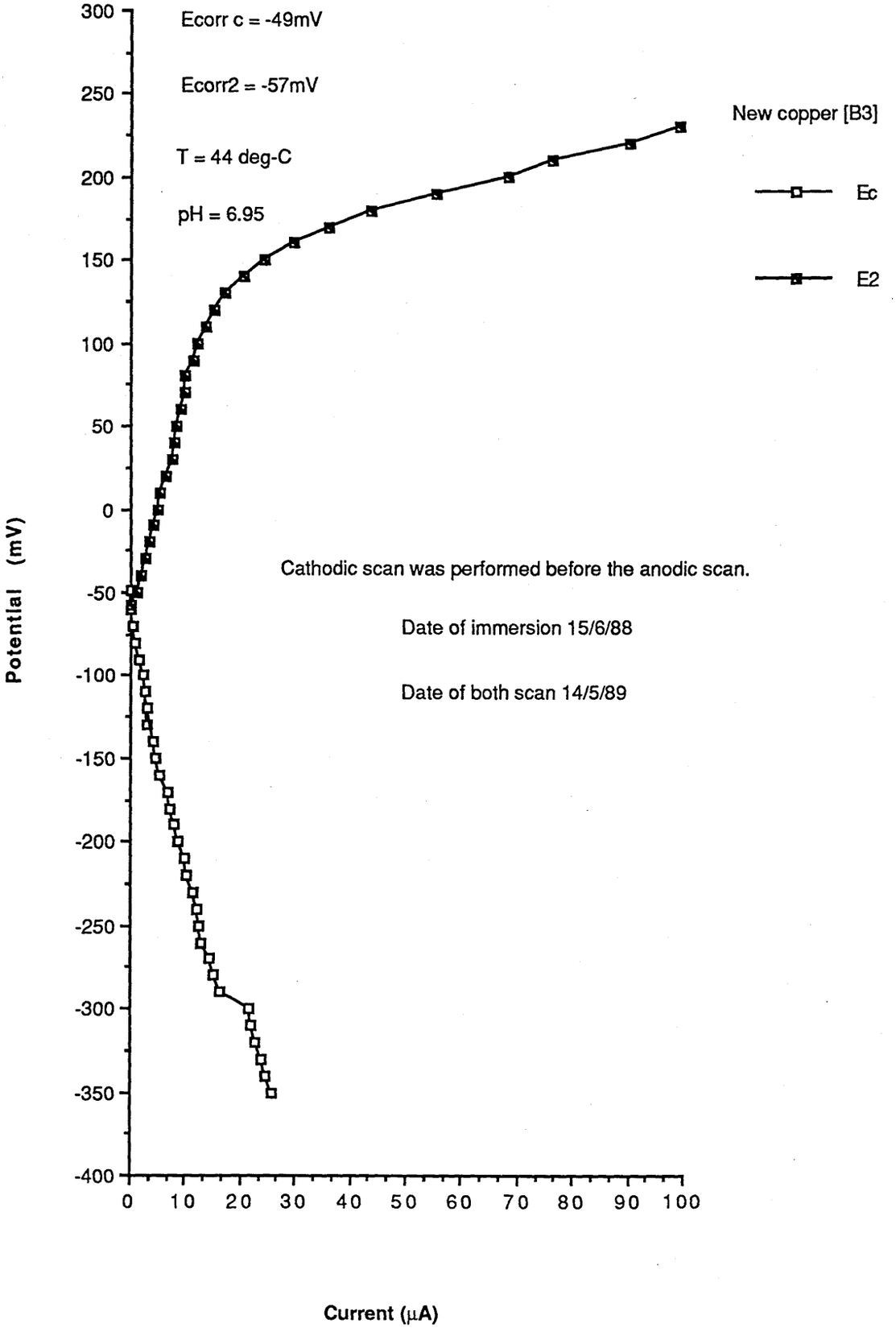
Normal hot water

Figure 25



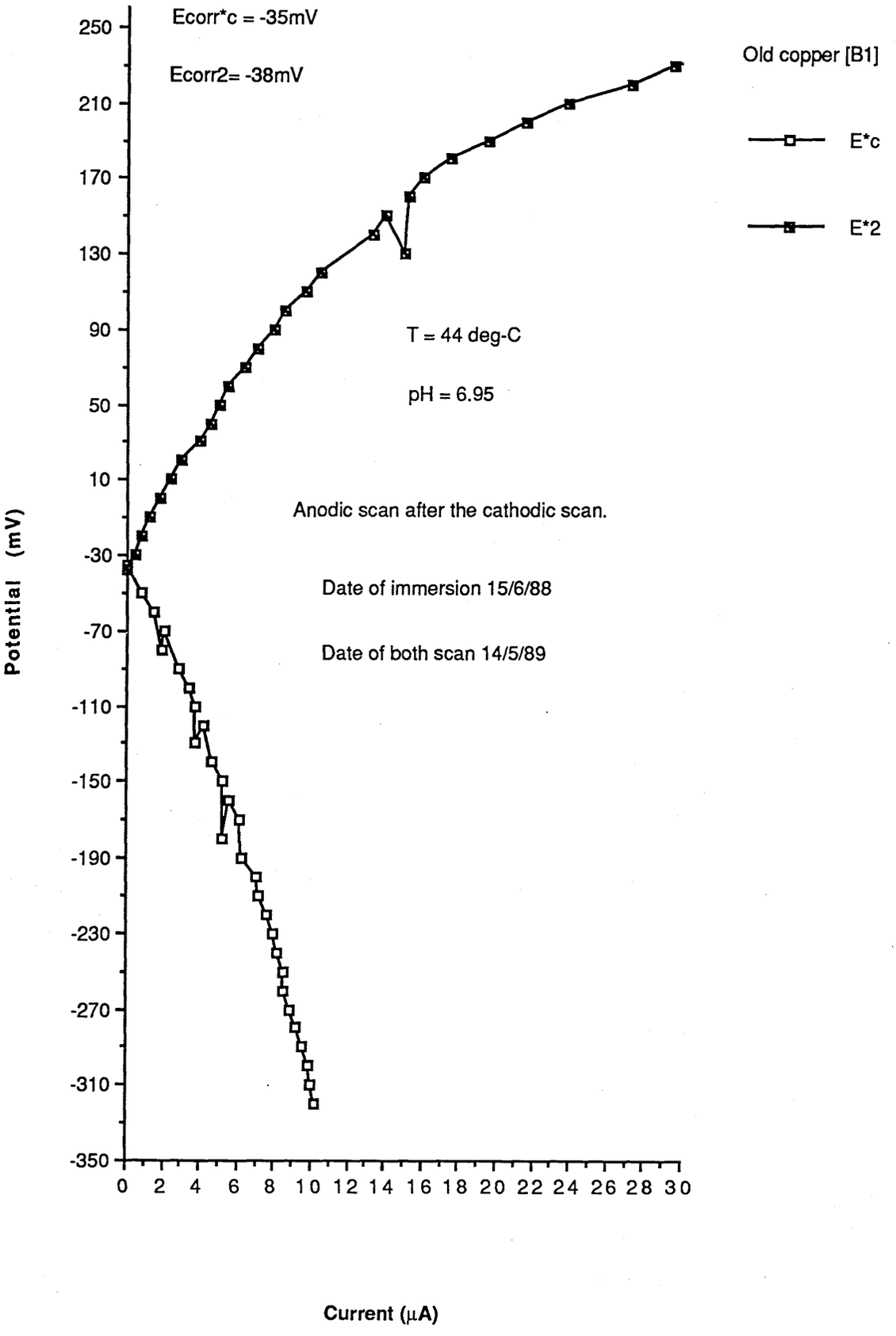
Normal hot water

Figure 25A



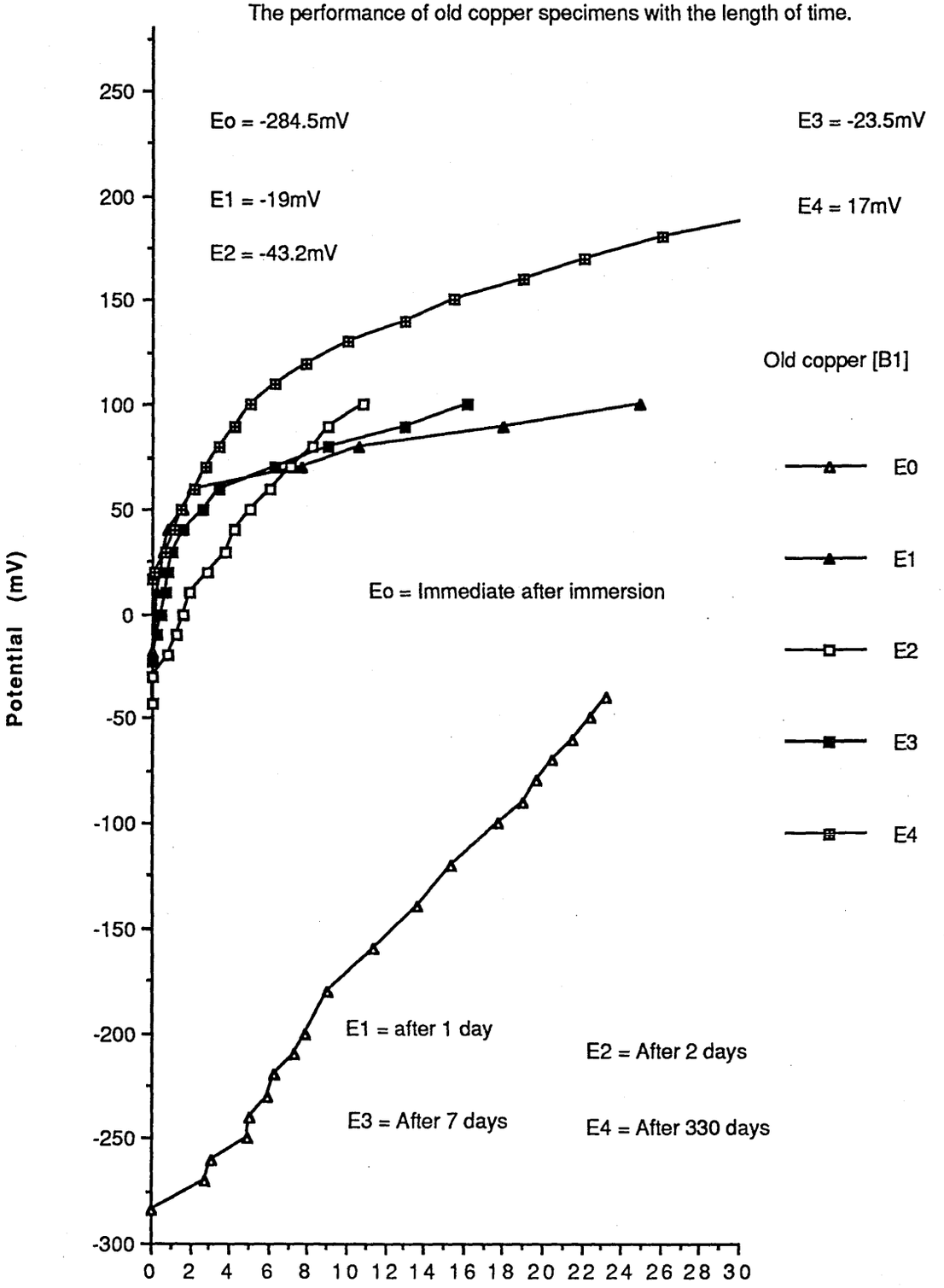
Normal hot water

Figure 26



Normal hot tap water Figure 27

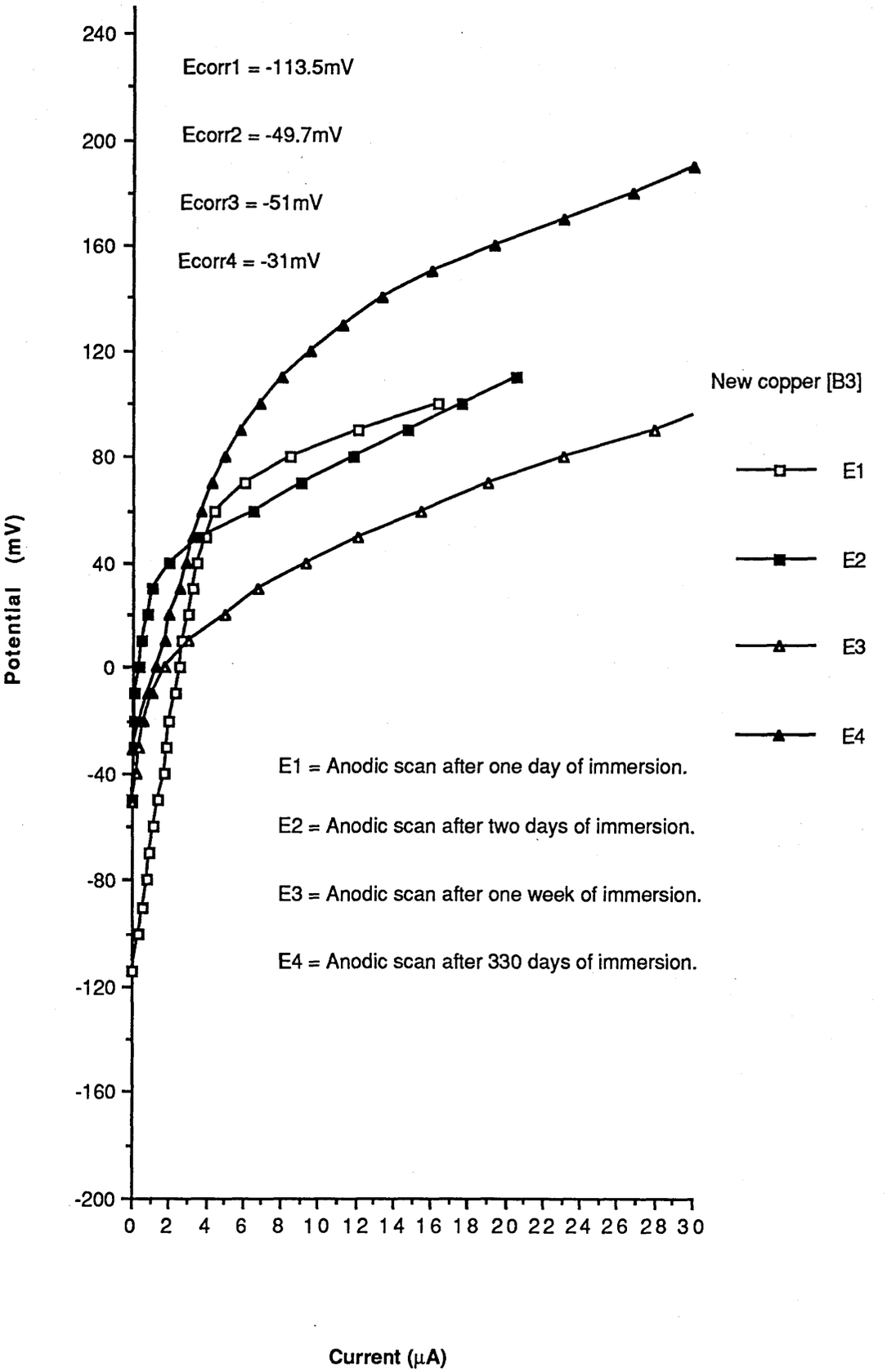
The performance of old copper specimens with the length of time.



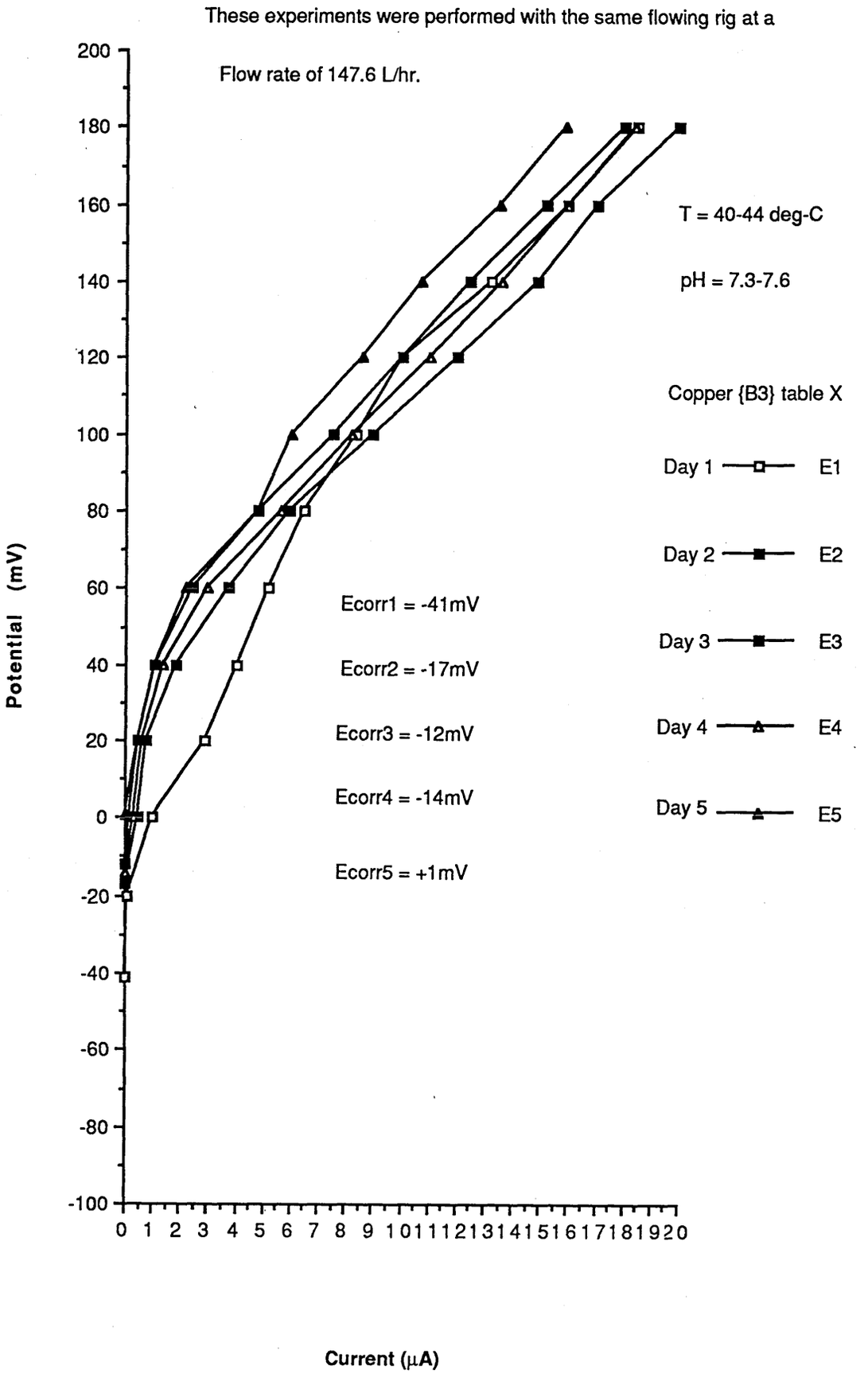
Normal hot water

Figure 28

Performance of new copper specimens with the length of time.

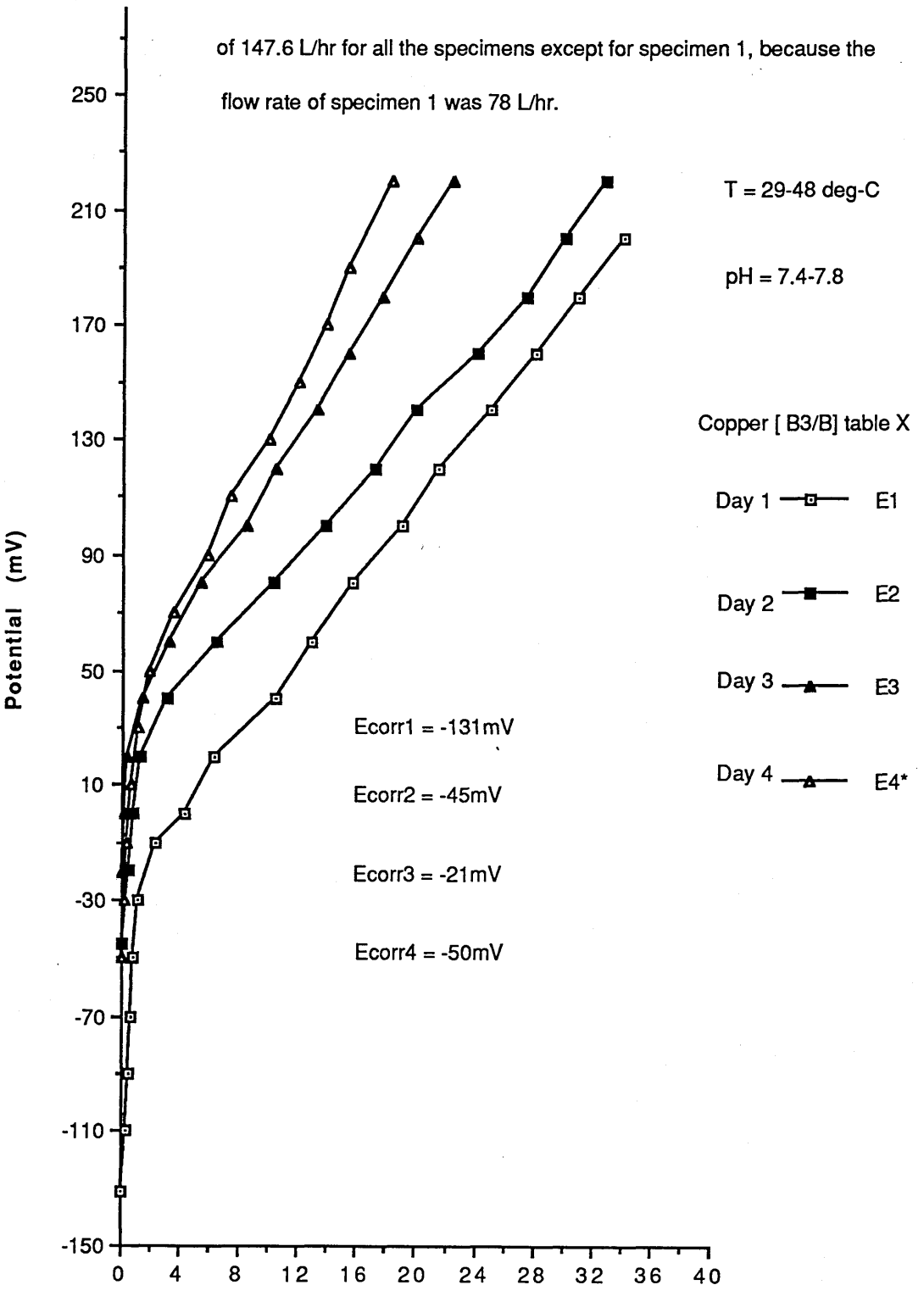


Normal hot water Figure 29

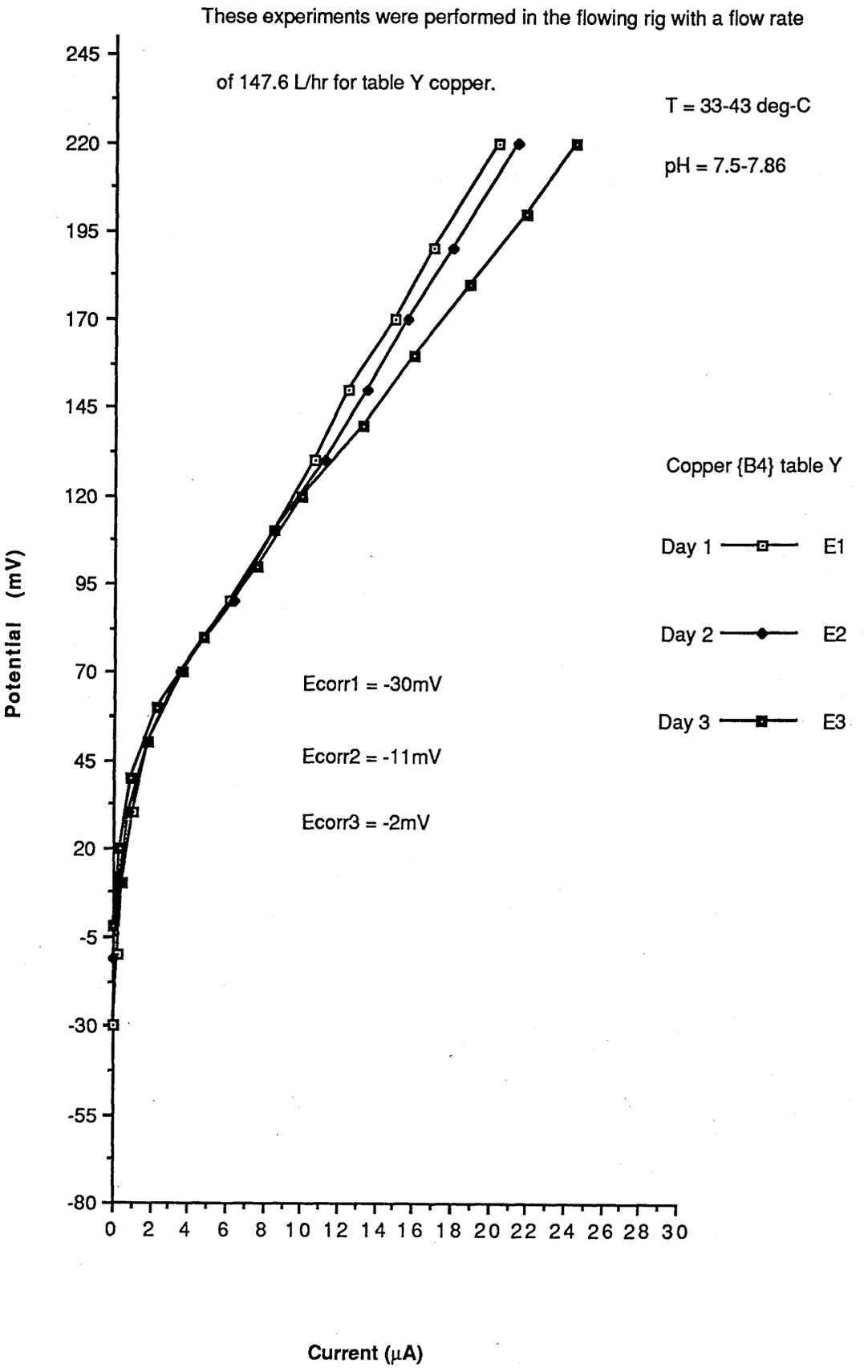


Normal hot water Figure 30

These experiments were carried out with the flowing rig at flow rate of 147.6 L/hr for all the specimens except for specimen 1, because the flow rate of specimen 1 was 78 L/hr.

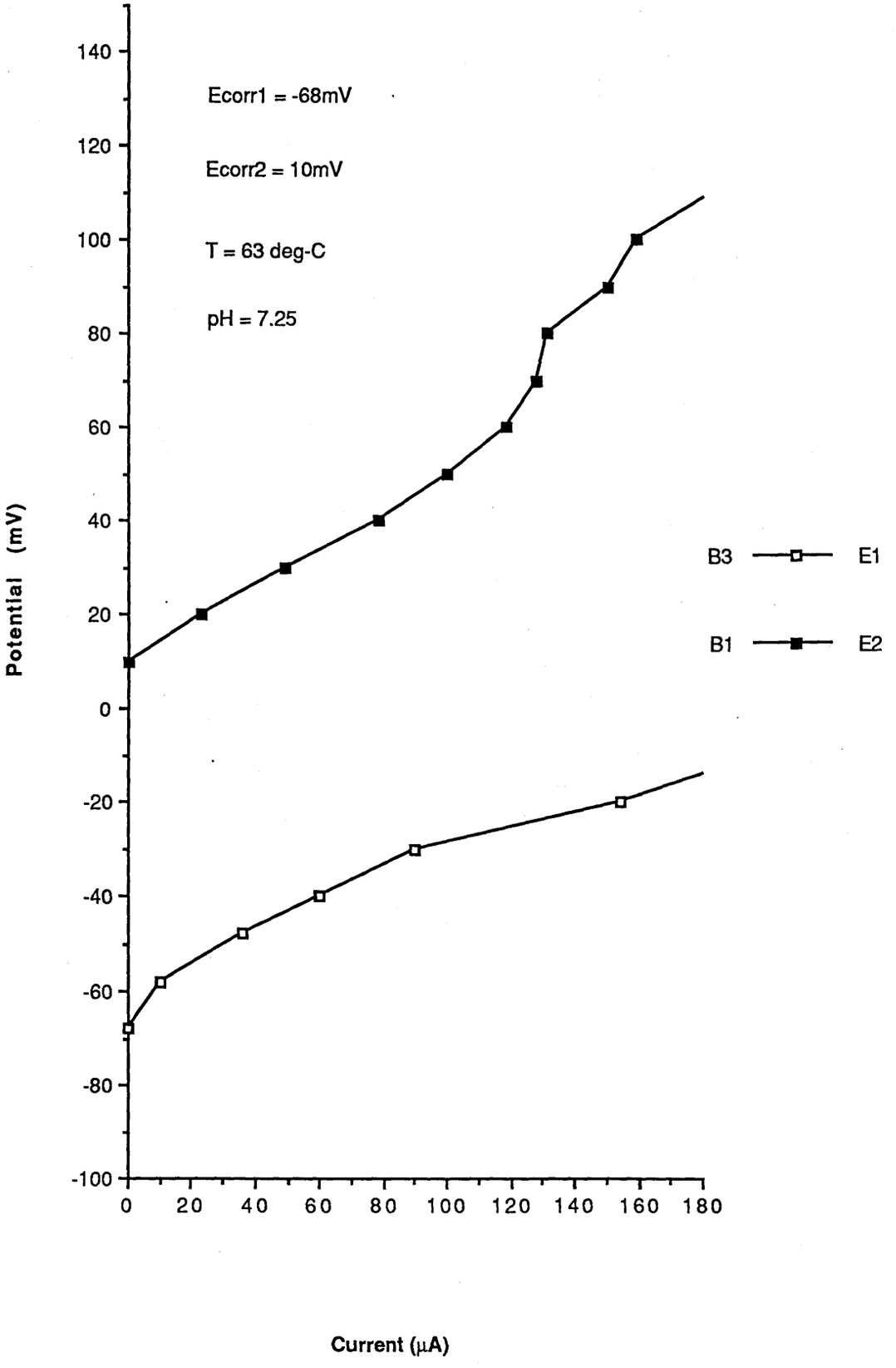


Normal hot water Figure 31



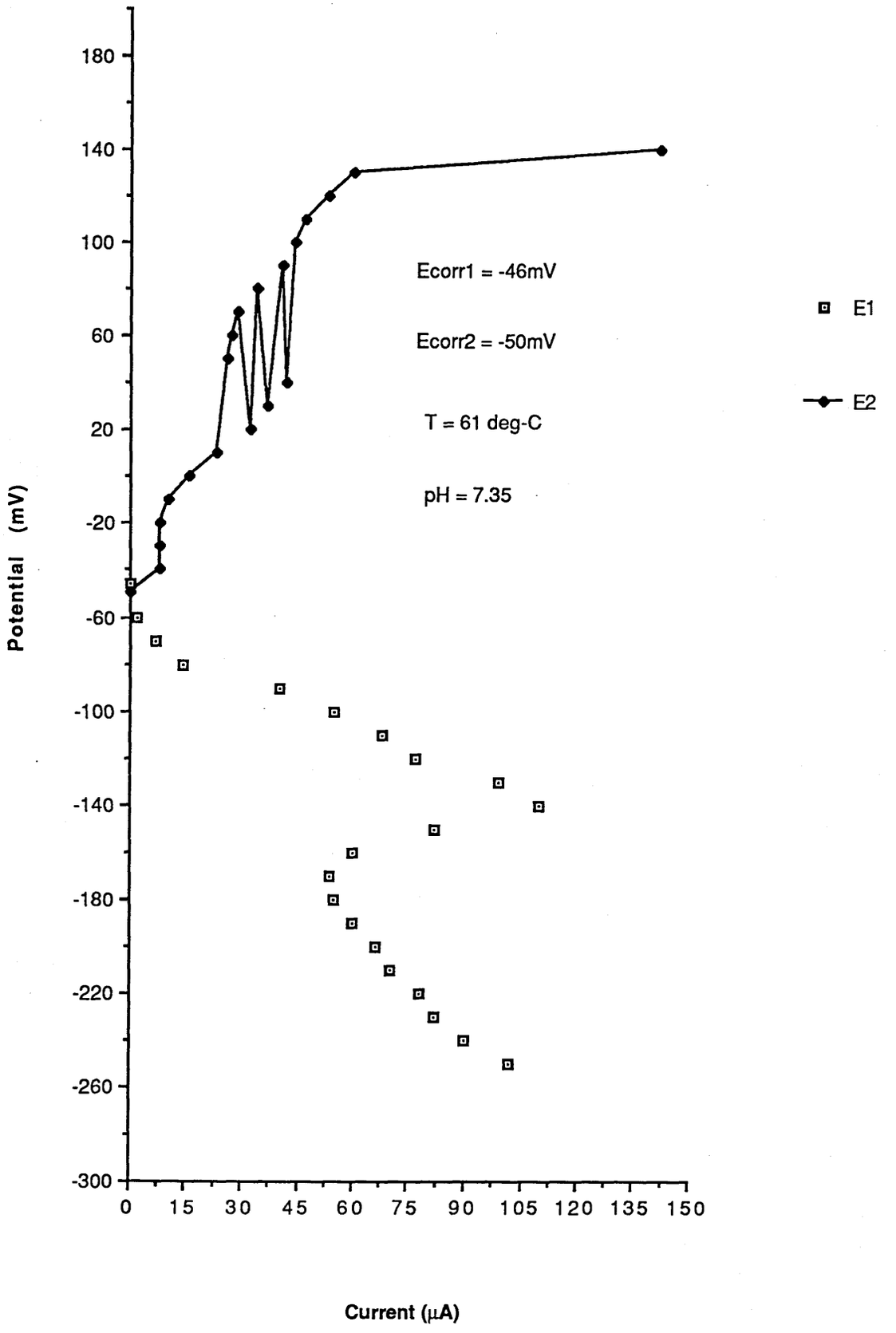
Moving hot water at 60 deg-C Figure 32

Anodic scan of both grades of copper specimens after immersion.



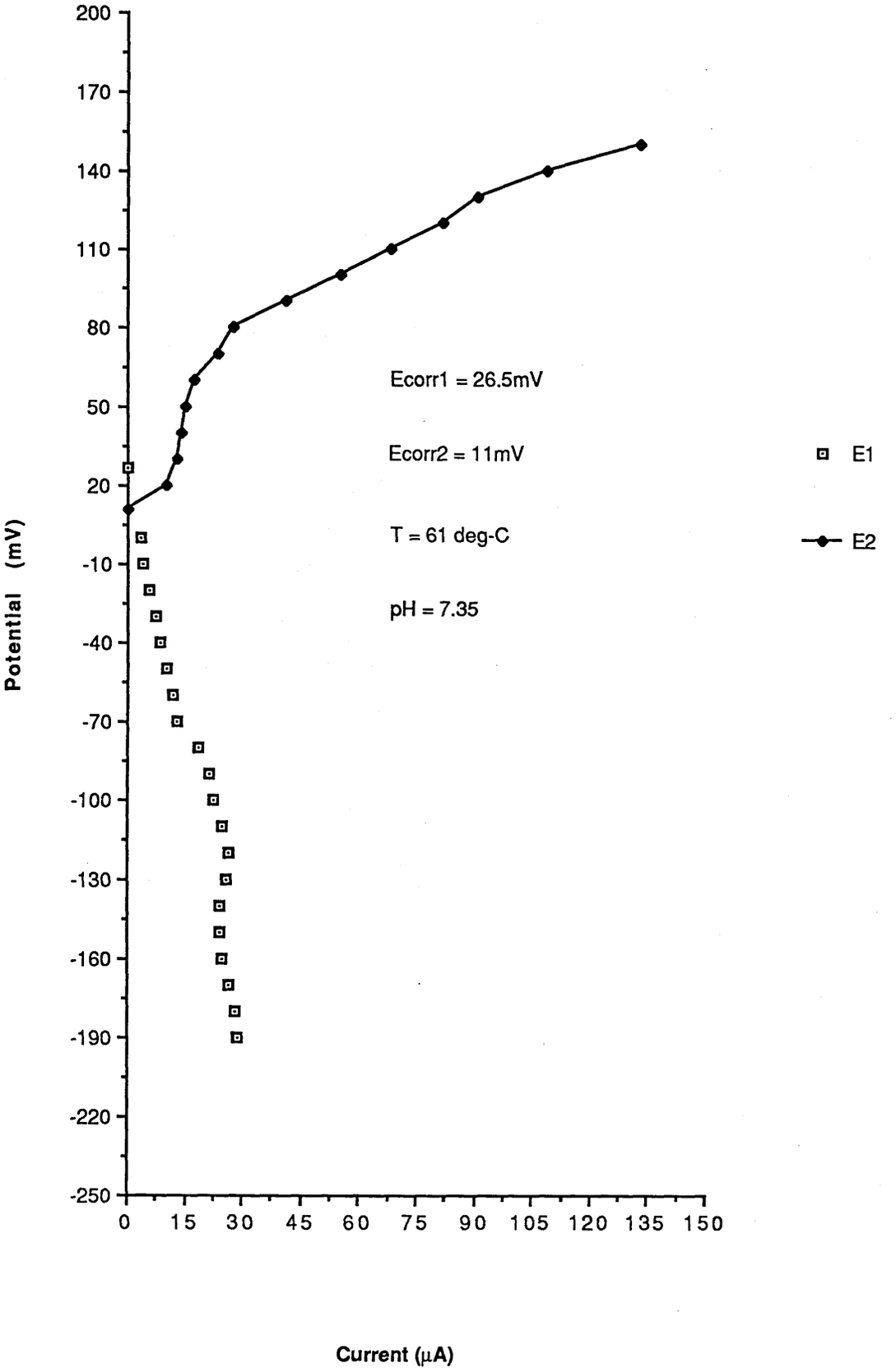
Moving hot water at 60 deg-C Figure 33

Cathodic scan followed by anodic scan of new copper specimen after immersion.



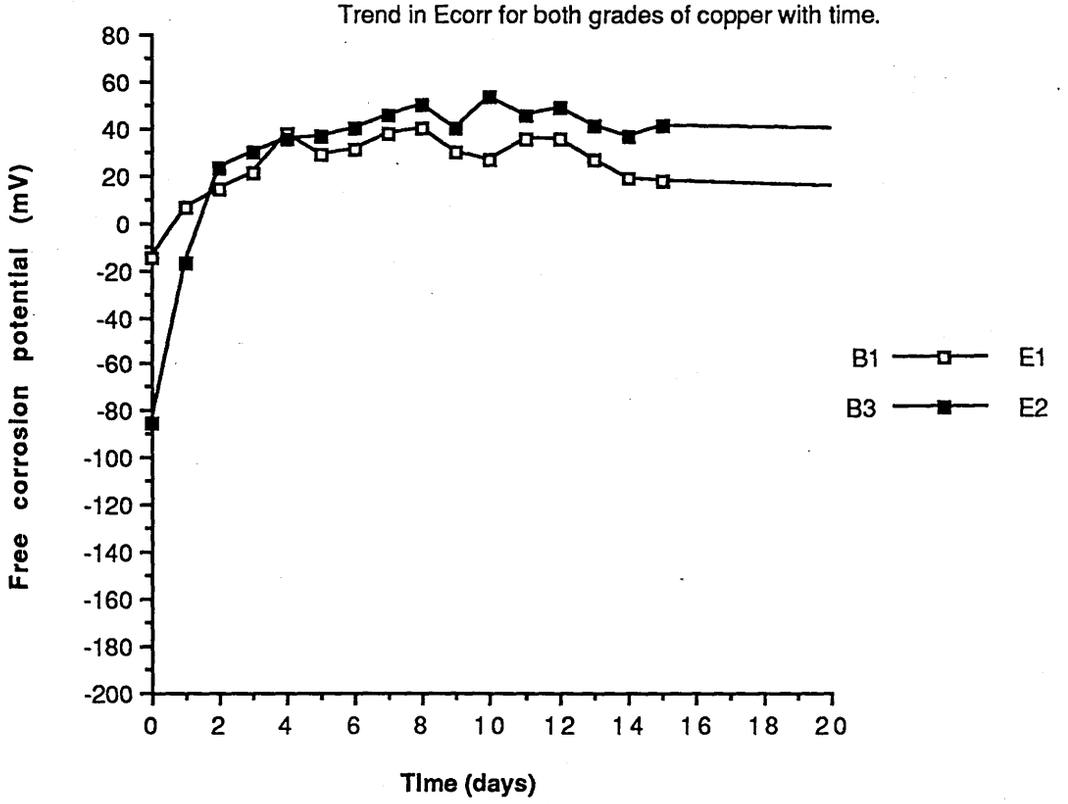
Moving hot water at 60 deg-C Figure 34

Cathodic scan followed by anodic scan of old copper specimen after immersion.



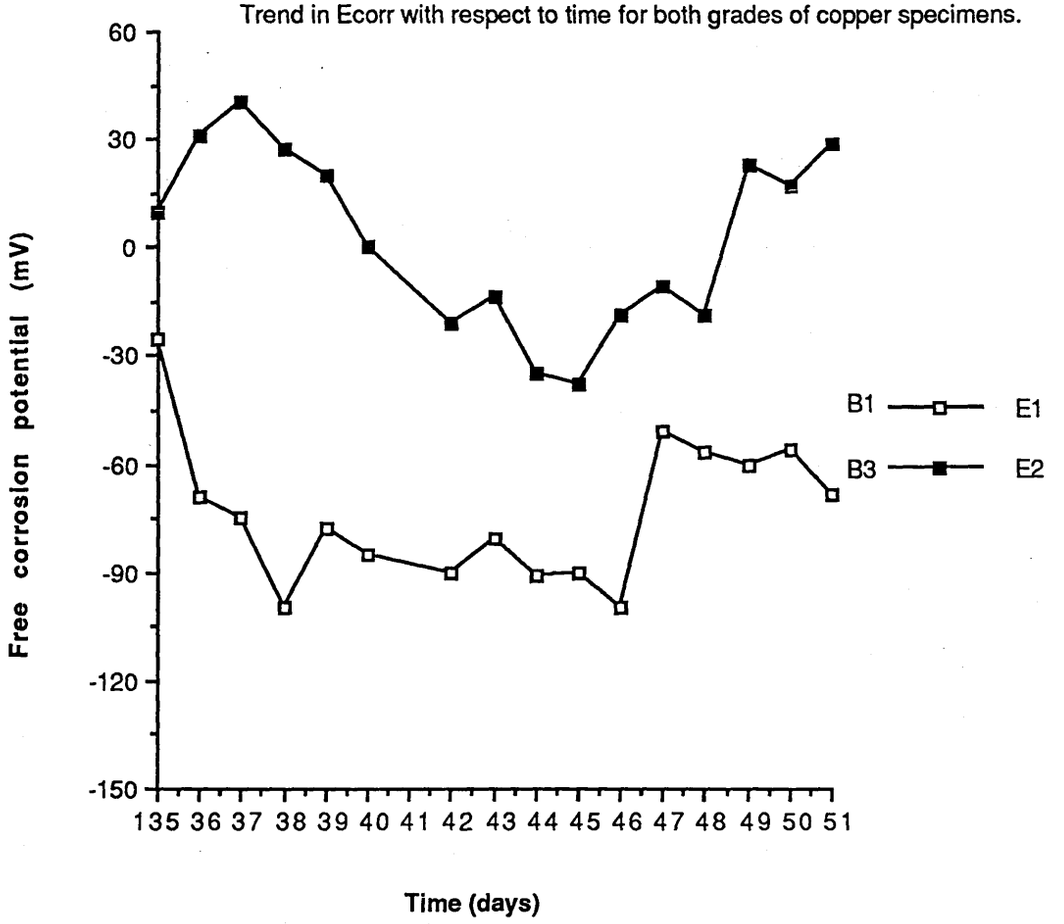
Hot water at 60 deg-C Figure 35

Trend in Ecorr for both grades of copper with time.



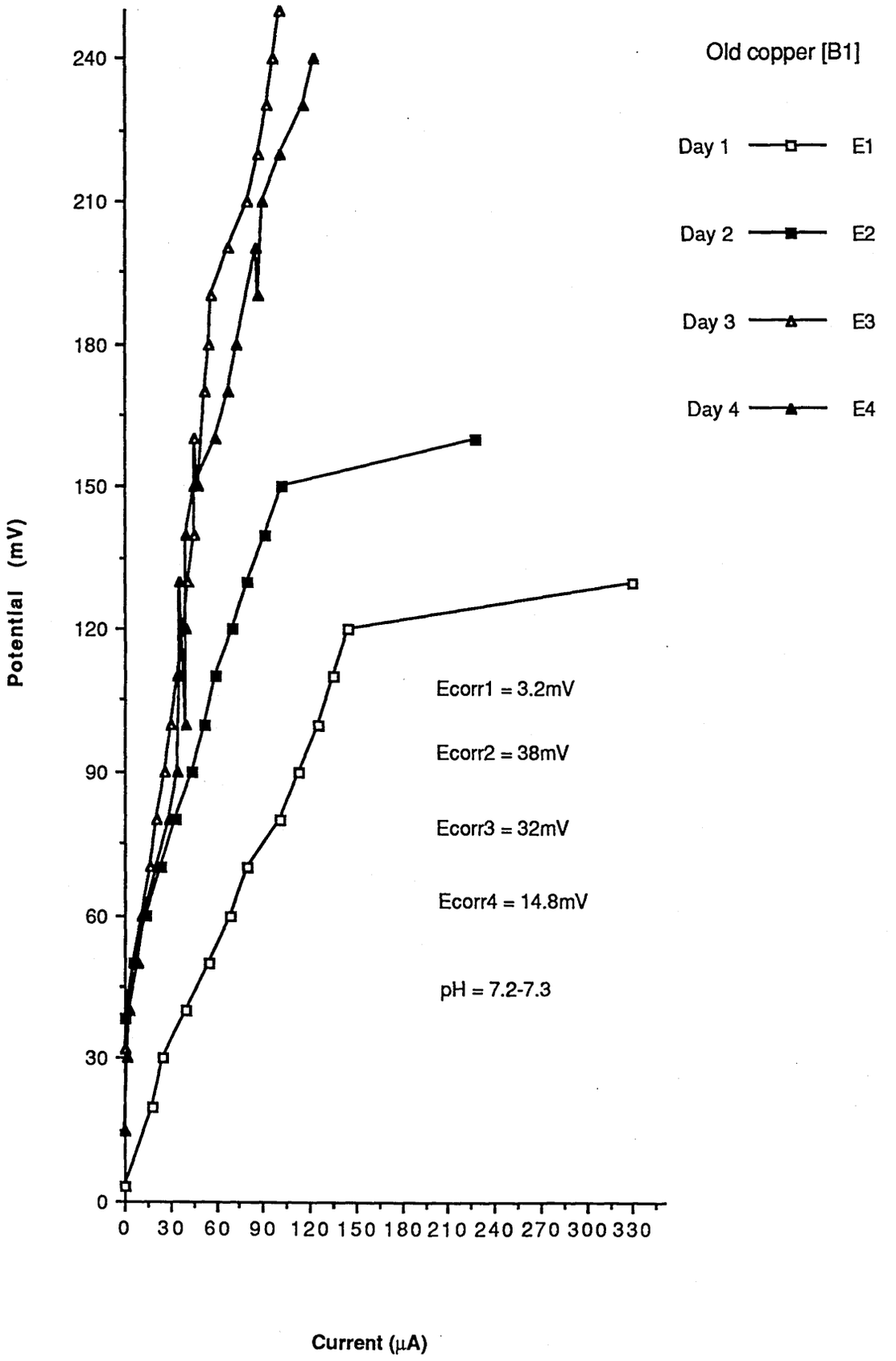
Hot water at 60 deg-C Figure 35a

Trend in Ecorr with respect to time for both grades of copper specimens.



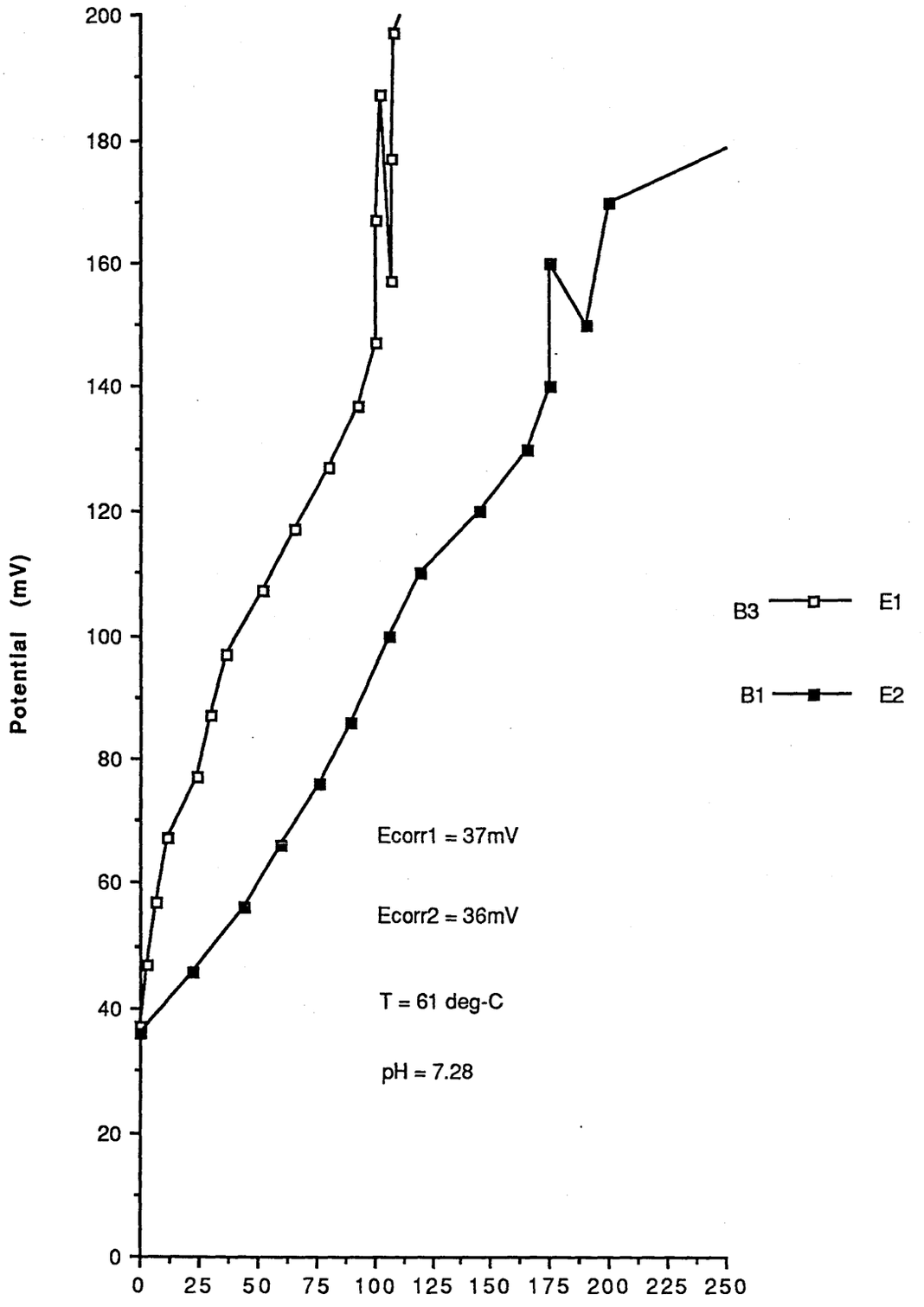
Moving hot water at 60 deg-C

Figure 36



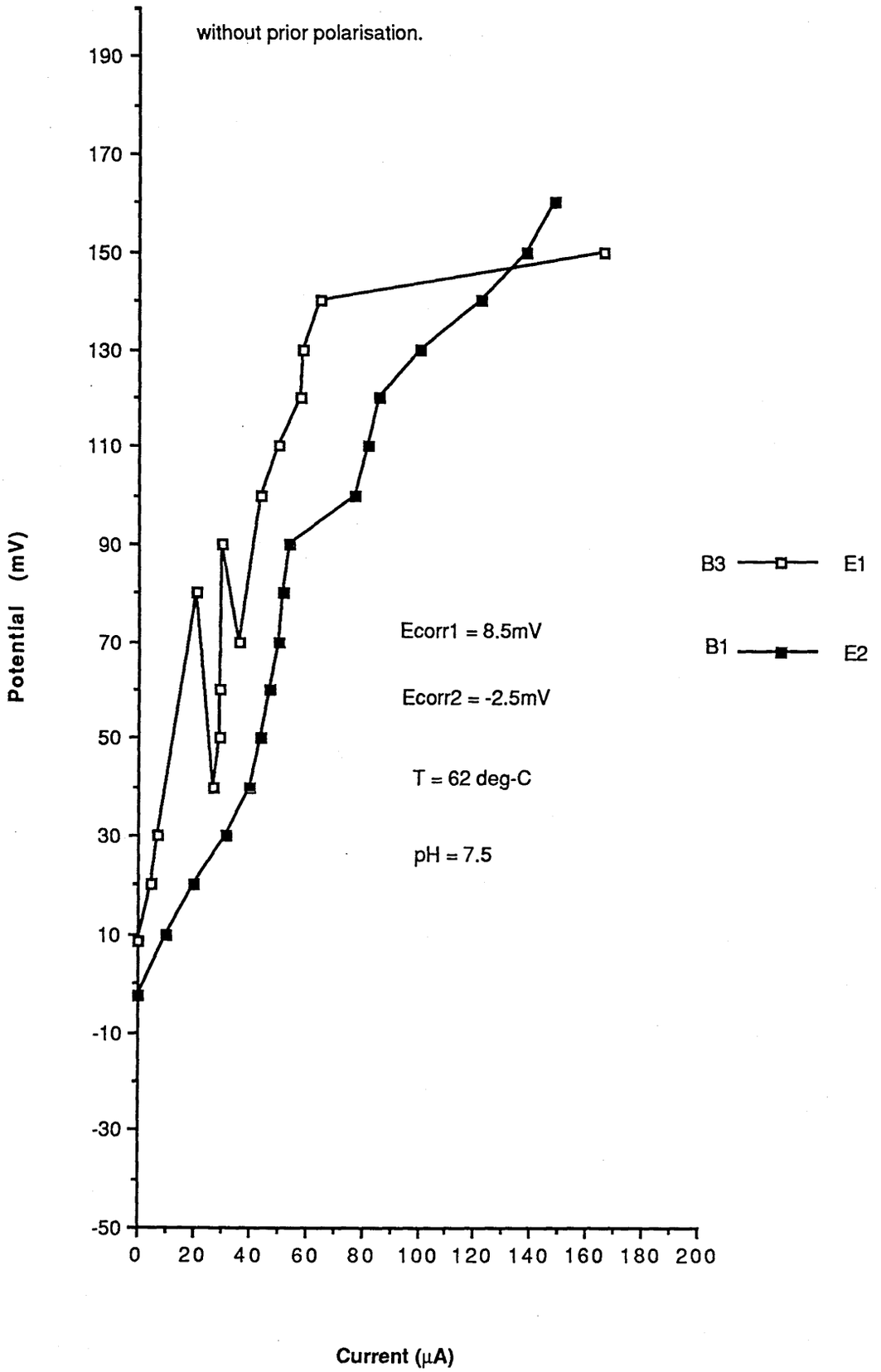
Moving hot water at 60 deg-C Figure 37

Anodic scan of both grades of copper specimen after one week of immersion.



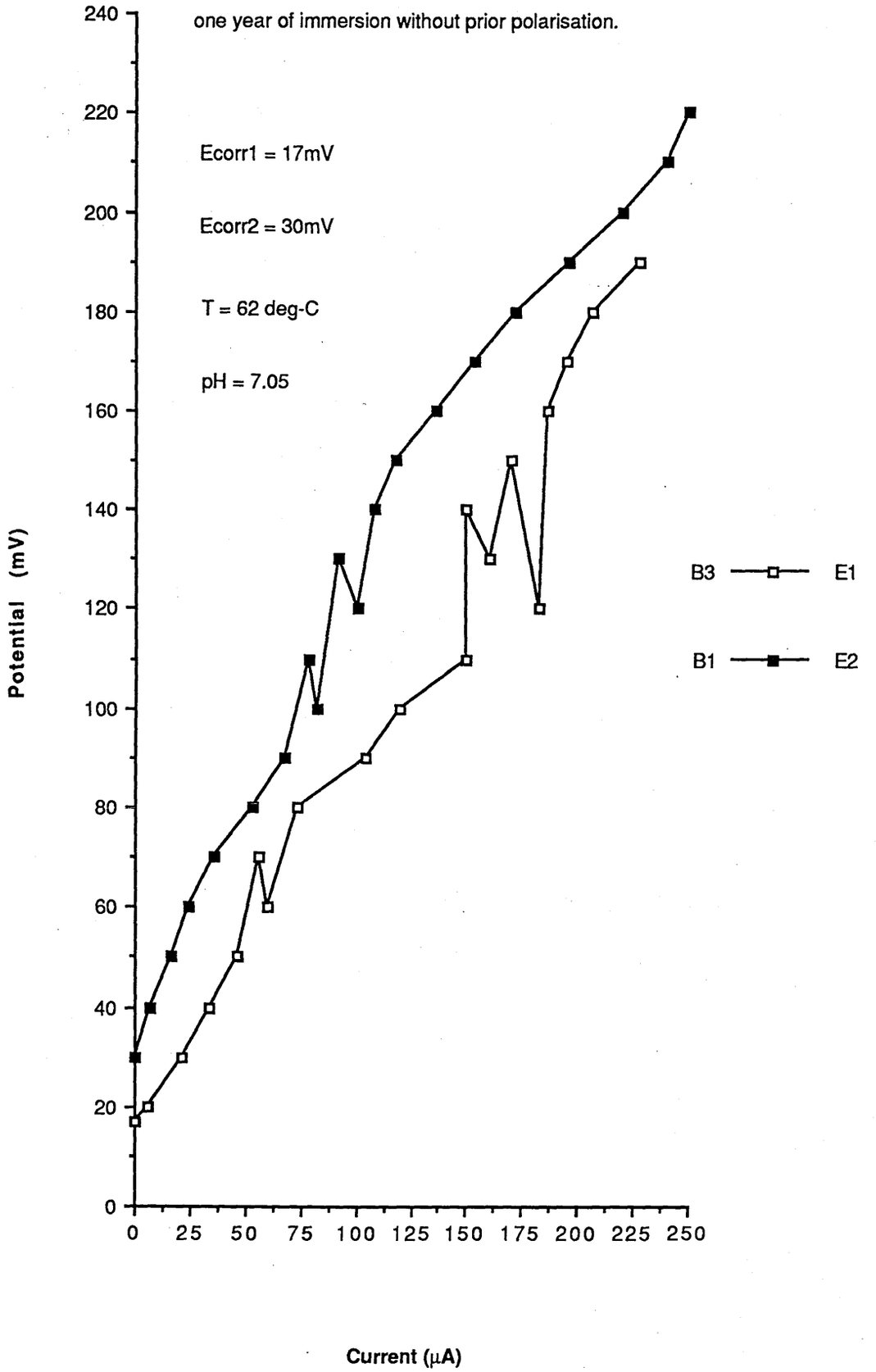
Moving hot water at 60 deg-C Figure 38

Anodic scan of both grades of copper specimens after five months of immersion without prior polarisation.



Moving hot water at 60 deg-C Figure 39

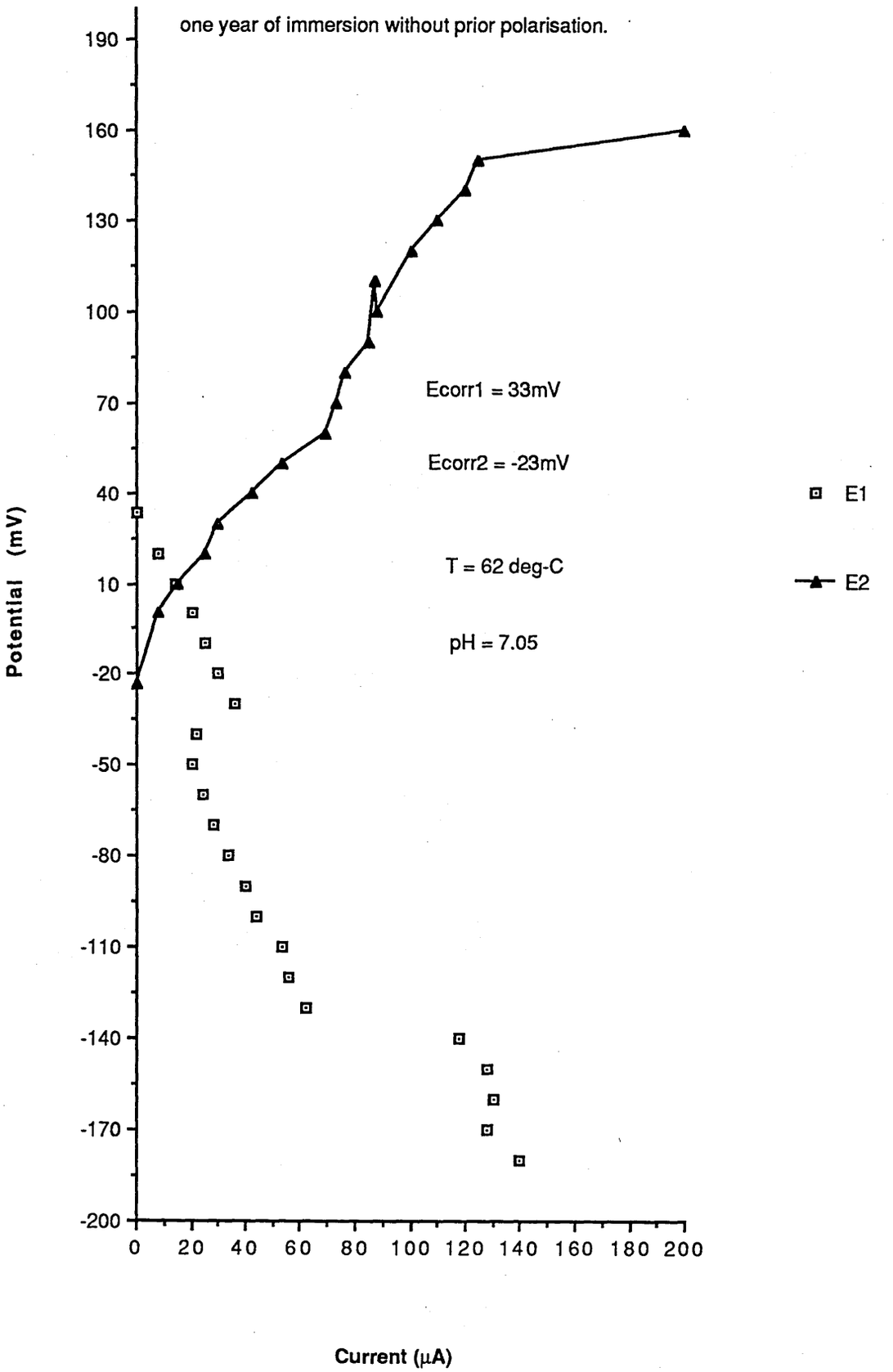
Anodic polarisation scan of both grades of copper specimens approximately after one year of immersion without prior polarisation.



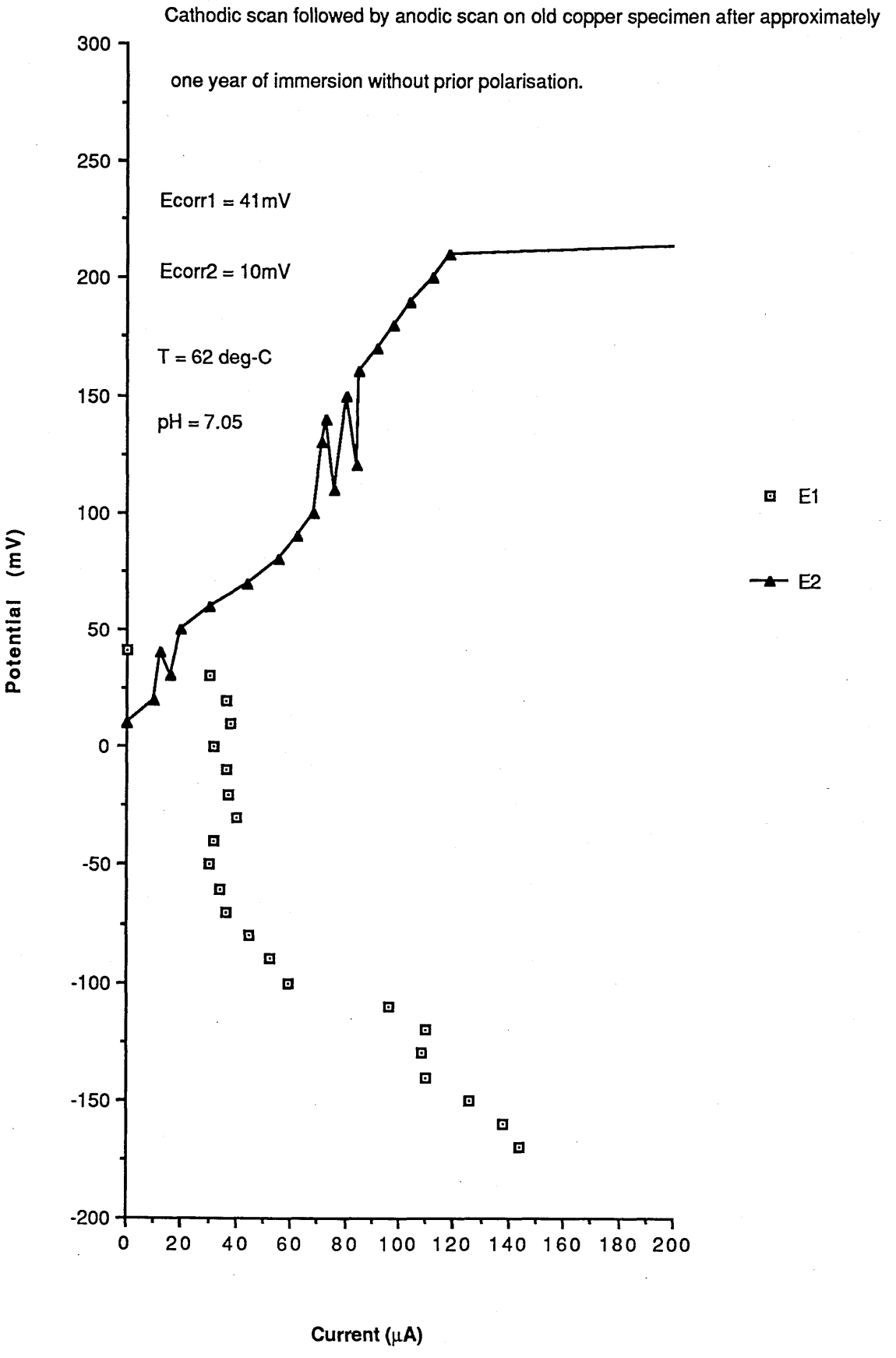
Moving hot water at 60 deg-C

Figure 40

Cathodic scan followed by anodic scan on new copper specimen after approximately one year of immersion without prior polarisation.

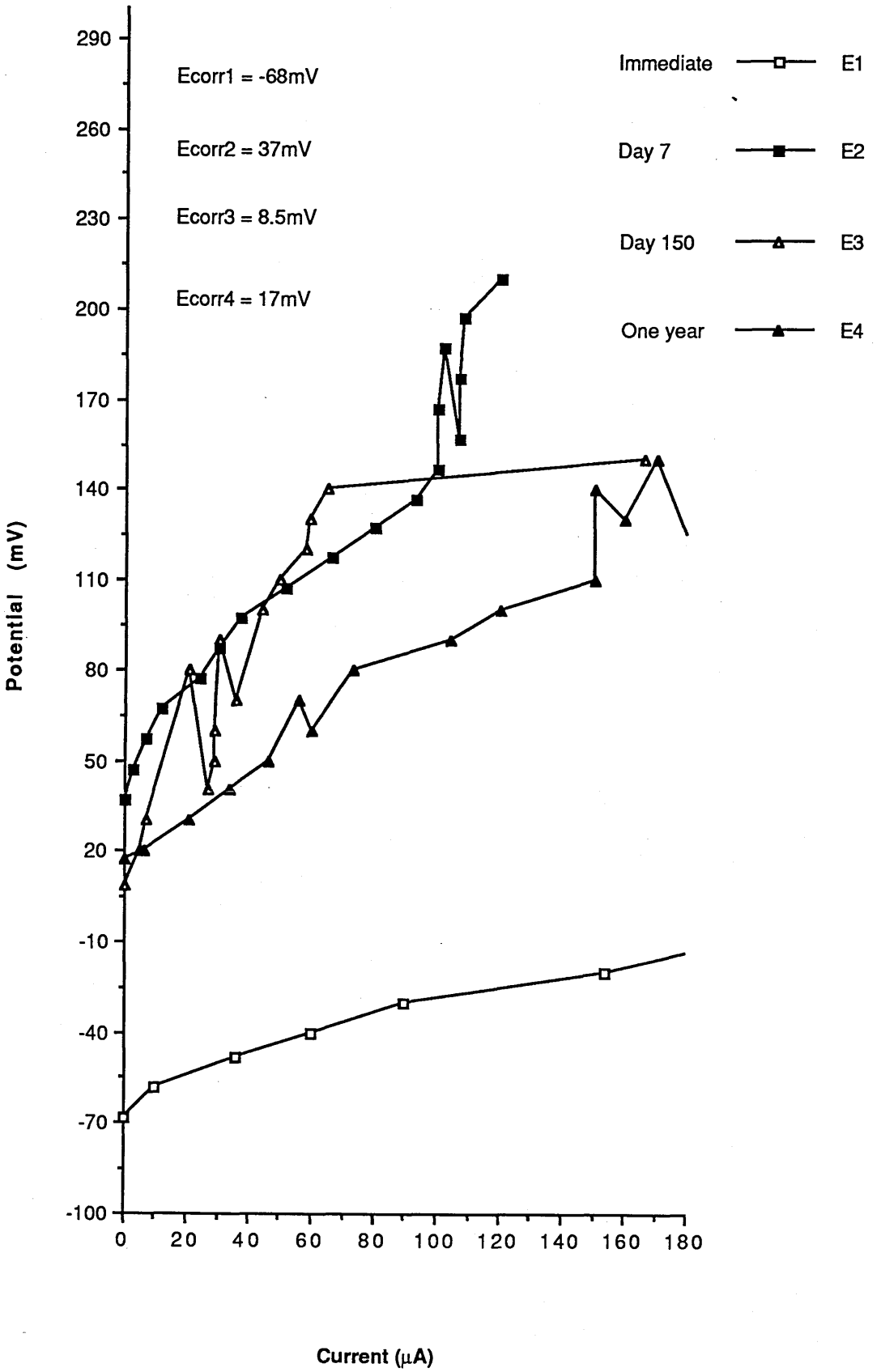


Moving hot water at 60 deg-C Figure 41



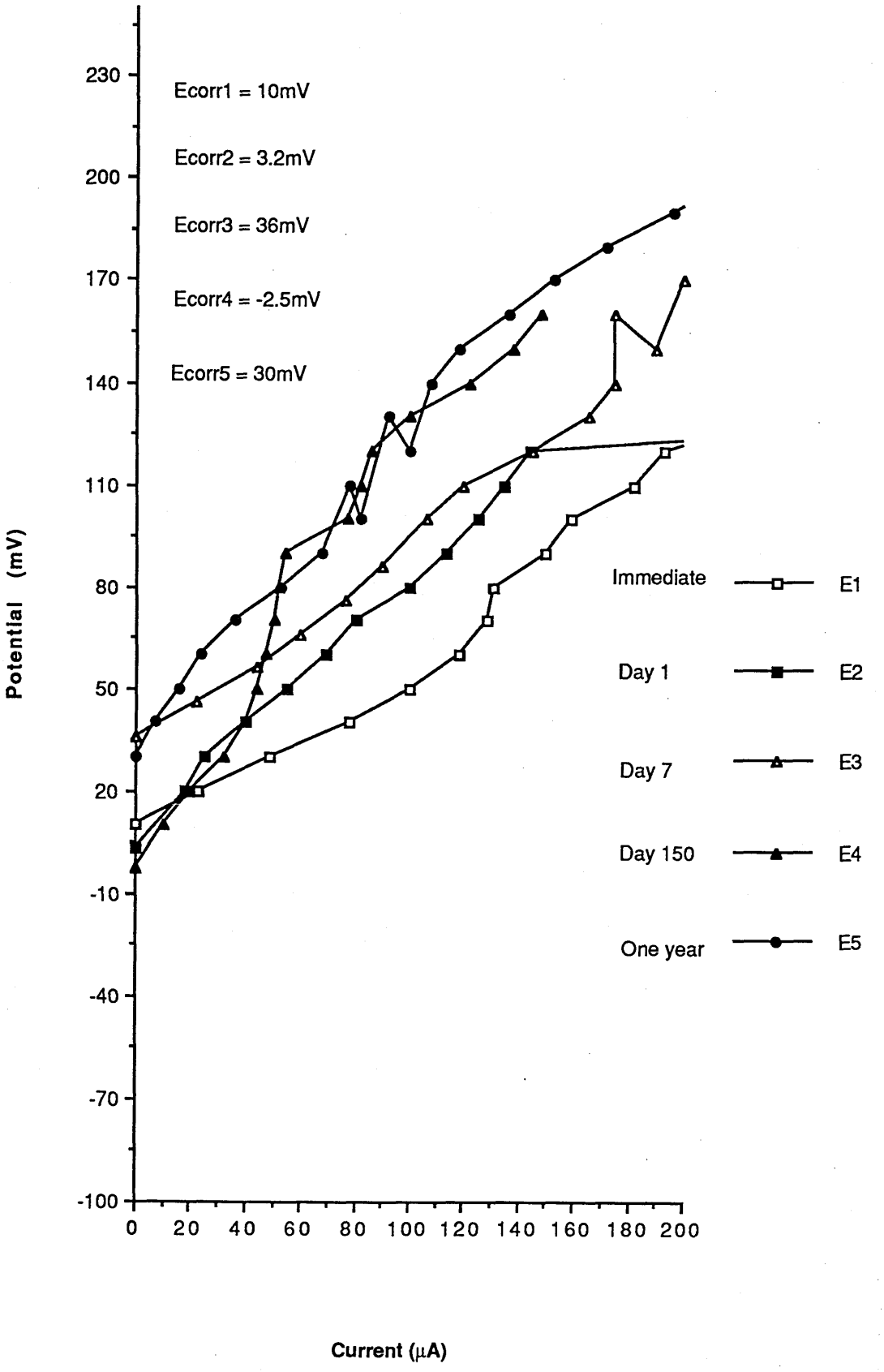
Moving hot water at 60 deg-C Figure 42

Performance of new copper {B3} with the length of immersion time.

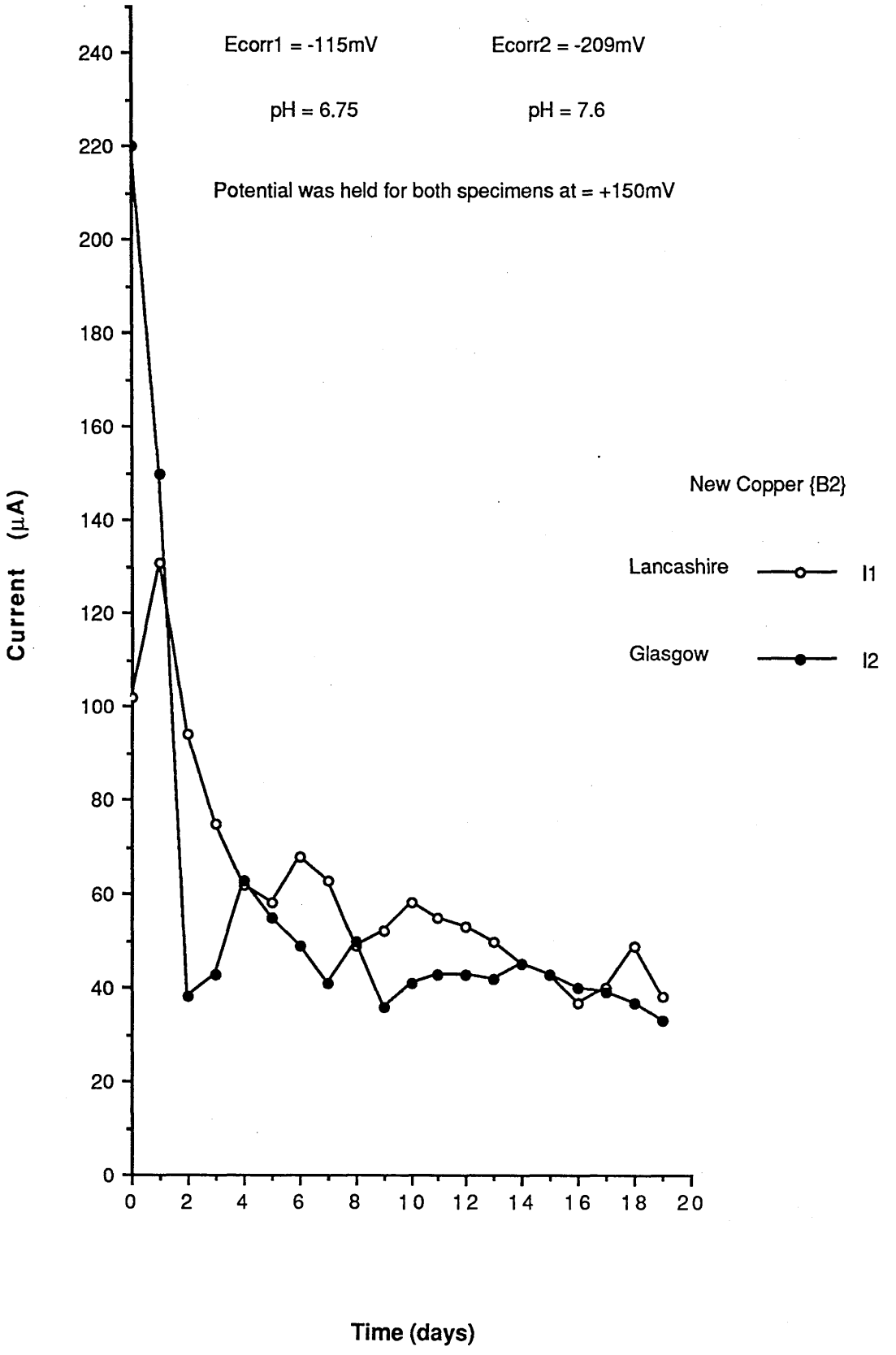


Moving hot water at 60 deg-C Figure 43

Performance of old copper [B1] with response to time.



Potential holding experiments Figure 44

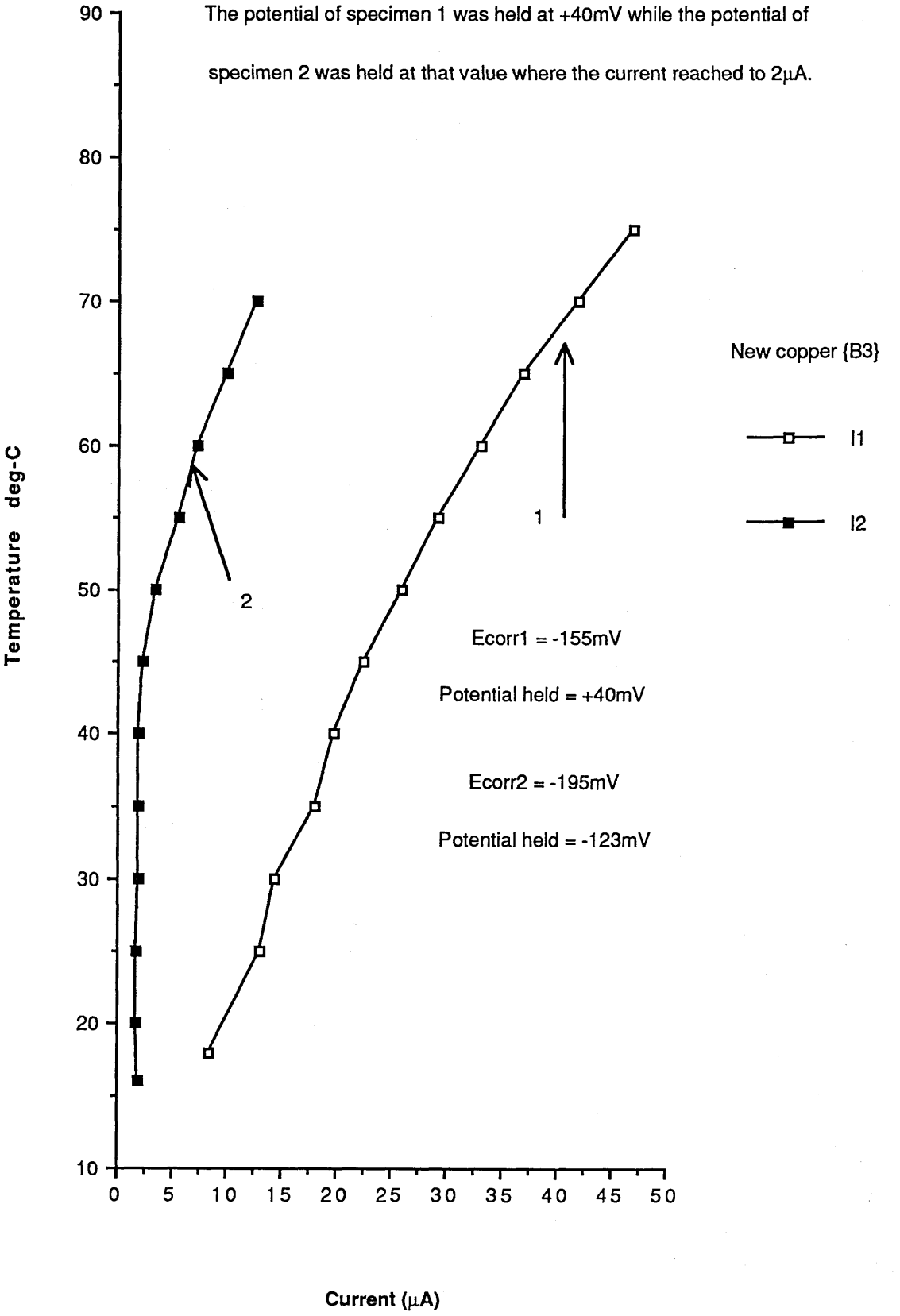


Current versus Temperature

Figure 45

Trend in current of two copper specimens with response to temperature.

The potential of specimen 1 was held at +40mV while the potential of specimen 2 was held at that value where the current reached to 2μA.

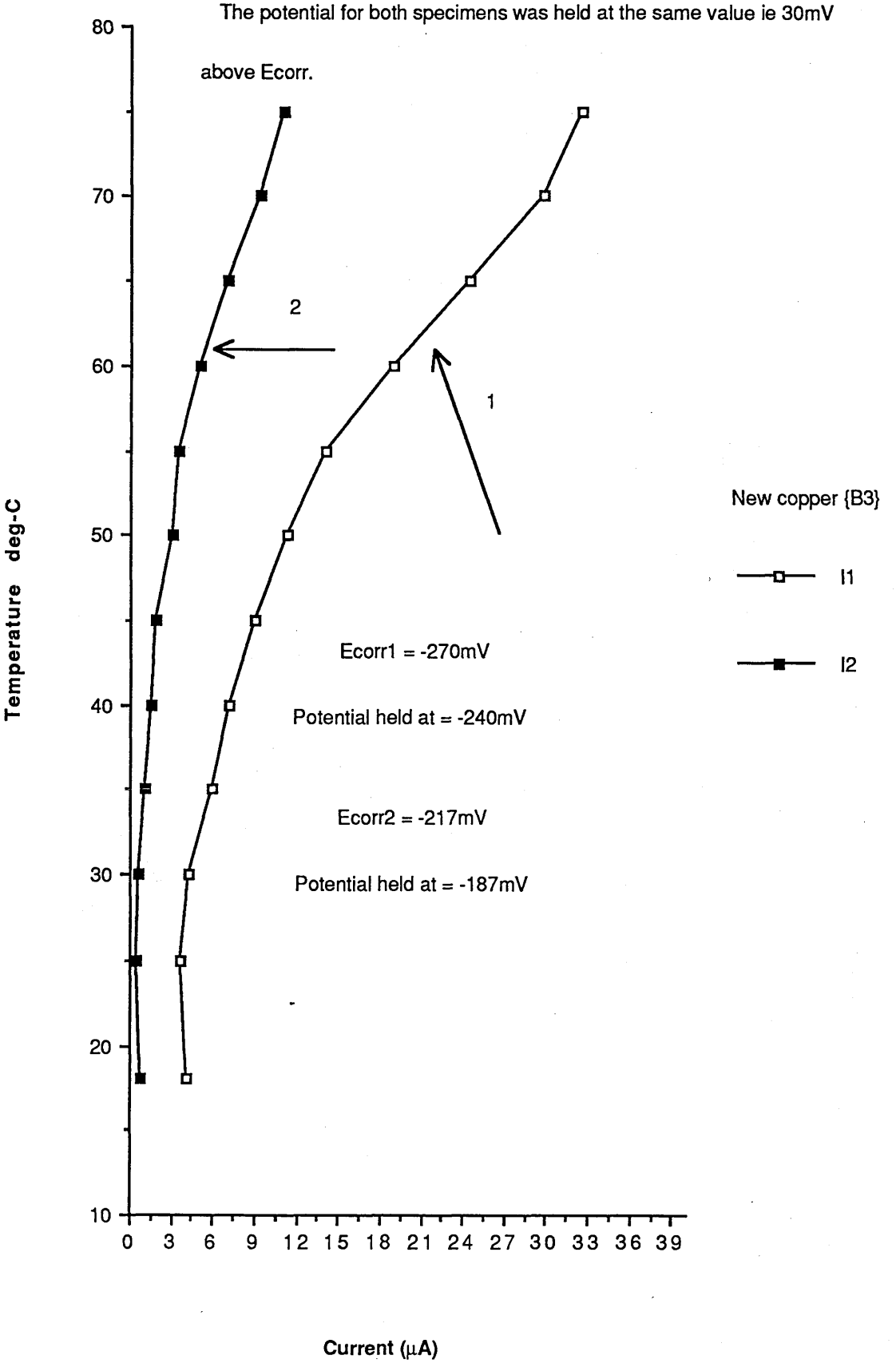


Potential holding experiment

Figure 46

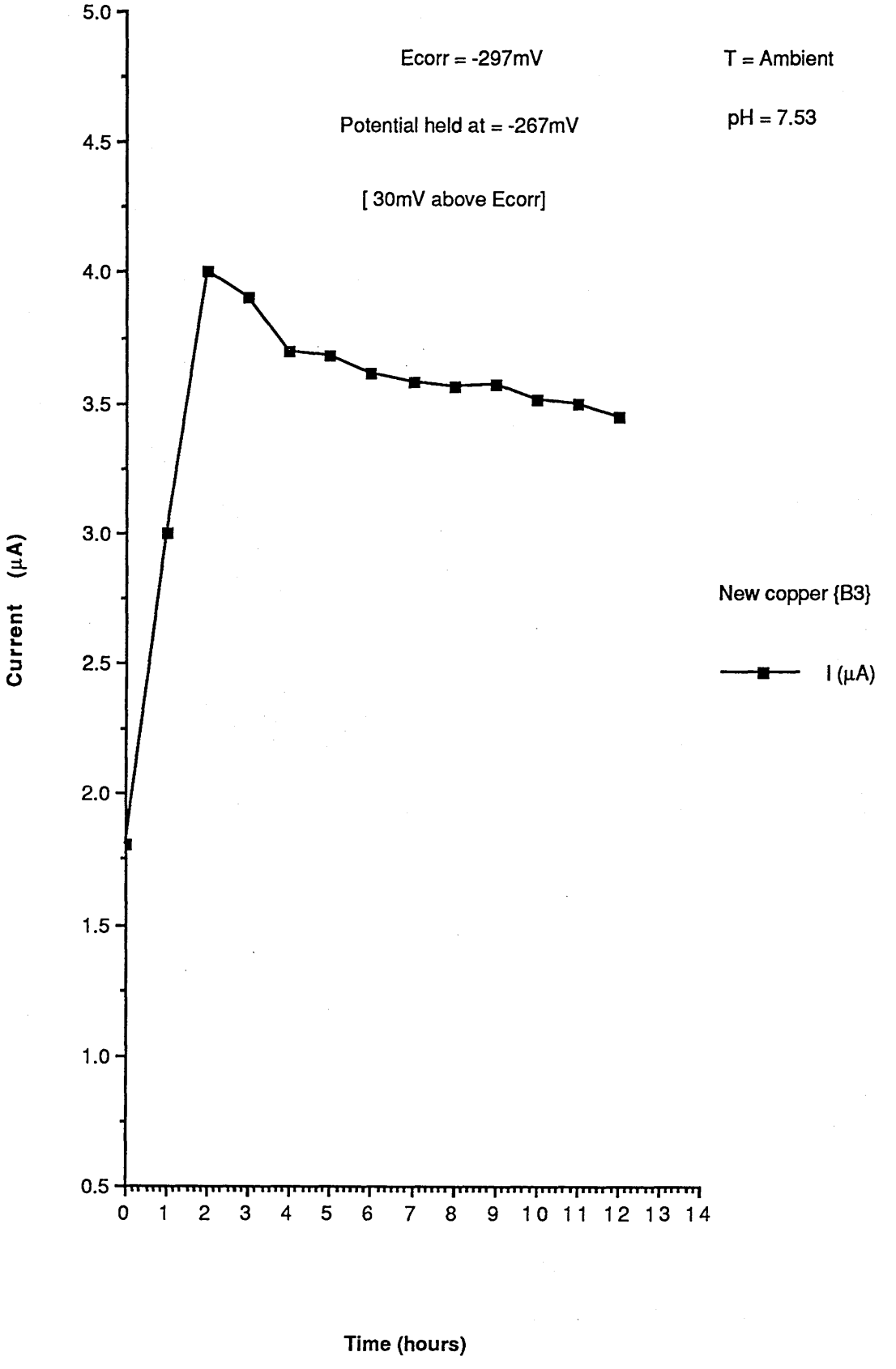
Trend in current of two copper specimens with response to temperature.

The potential for both specimens was held at the same value ie 30mV above Ecorr.



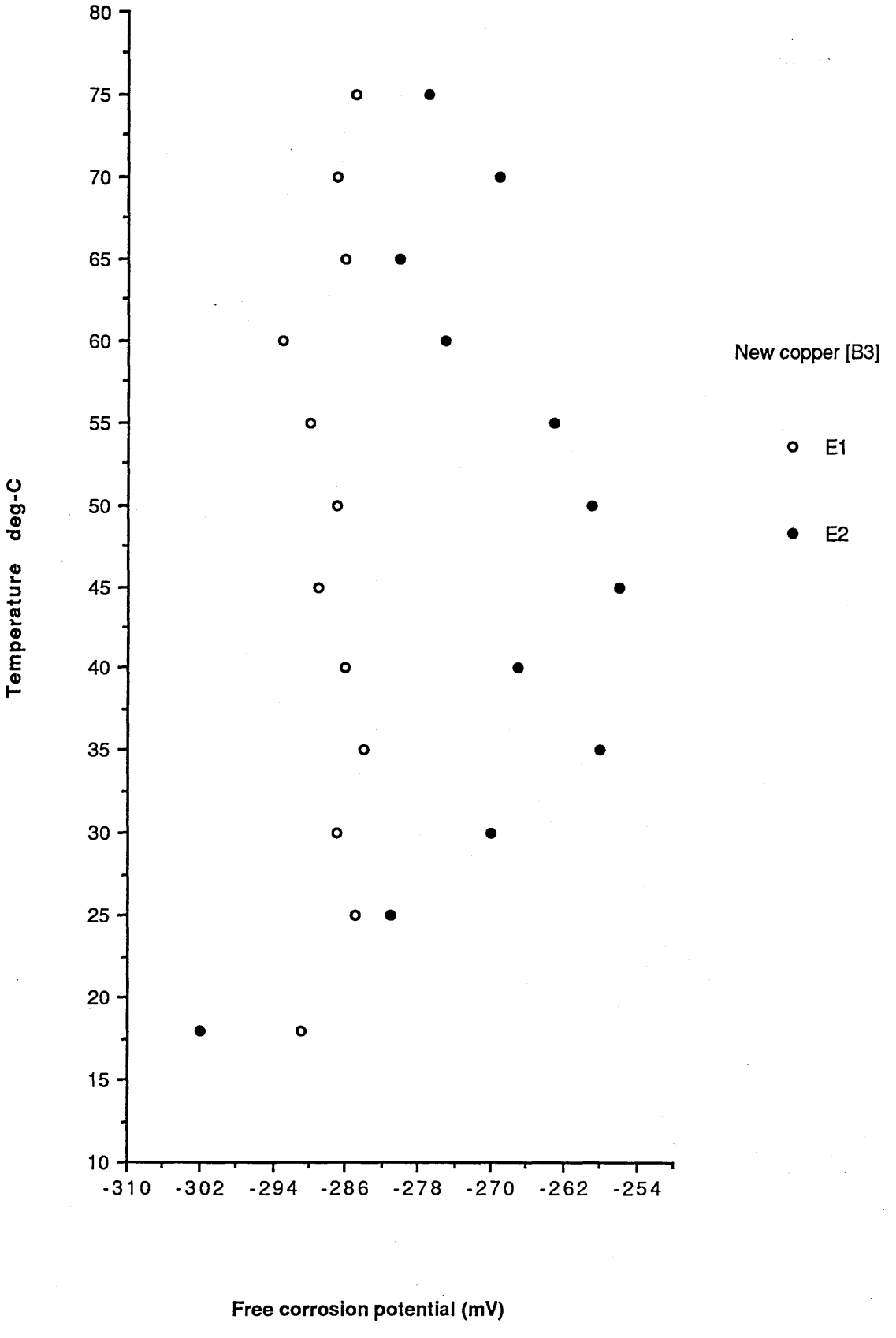
Potential holding experiment Figure 47

Trend in current of new copper specimen with respect to time.



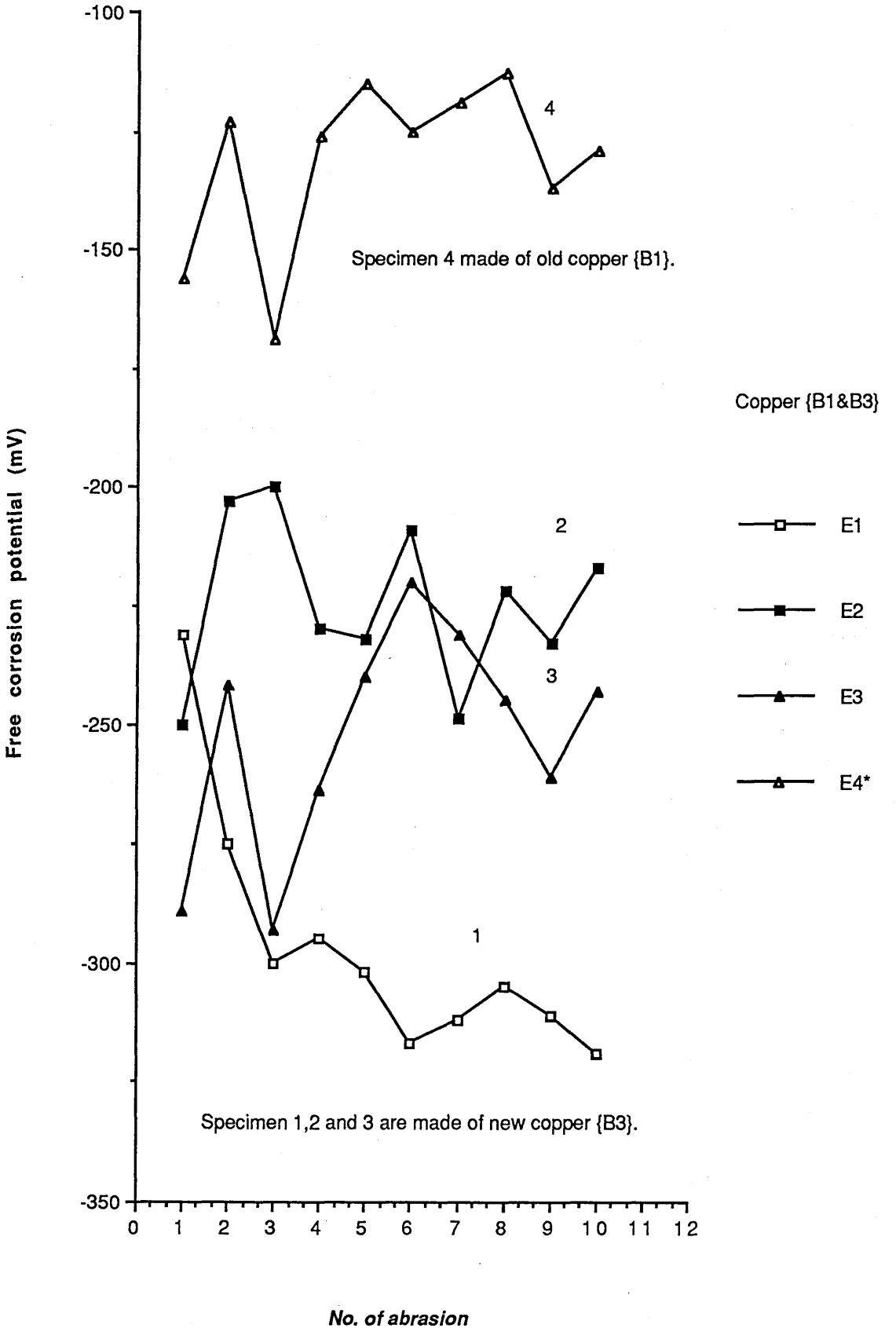
Potential versus Temperature Figure 48

Trend in free corrosion potential with respect to temperature.

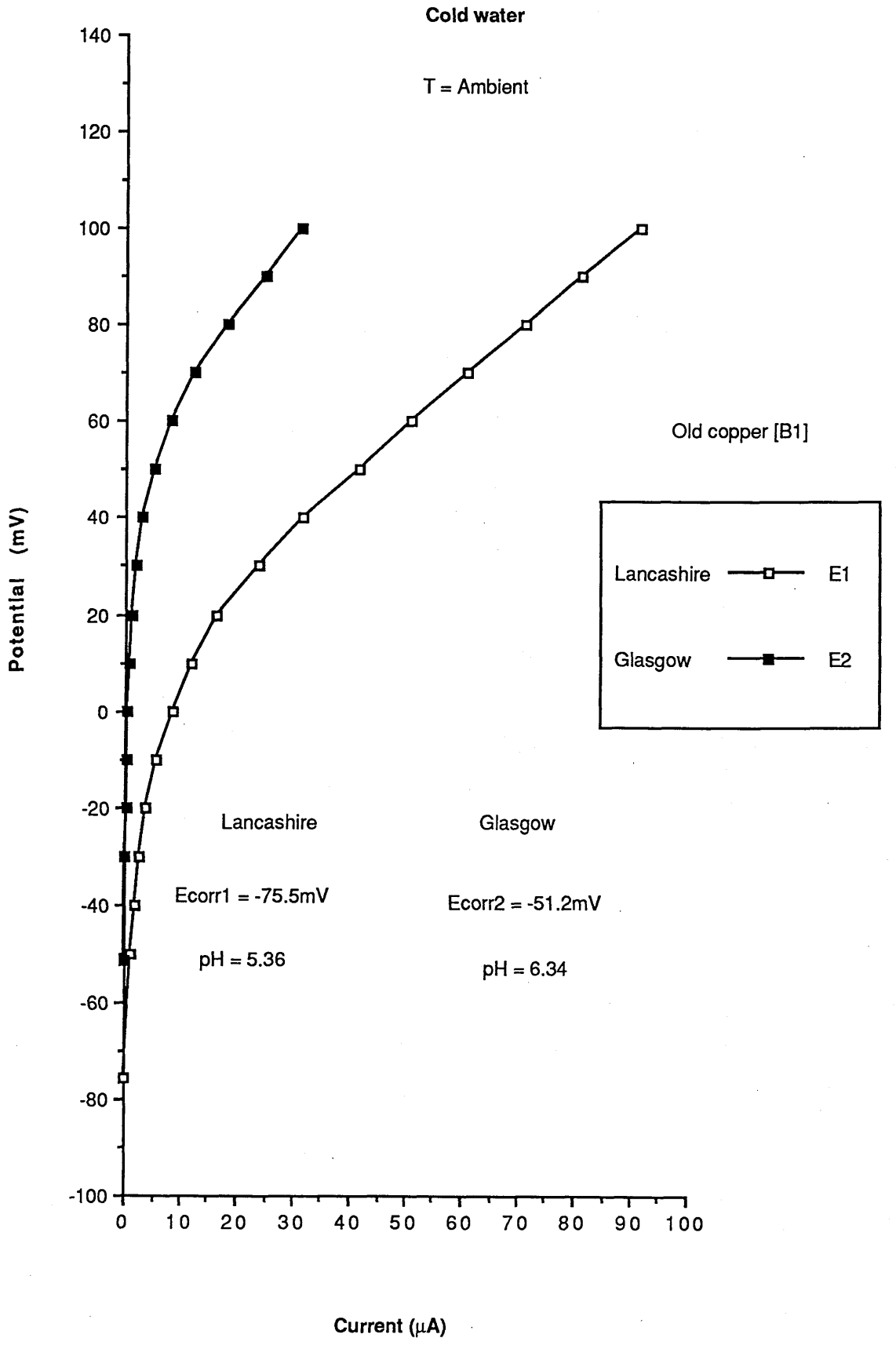


Potential versus Abrasion Figure 49

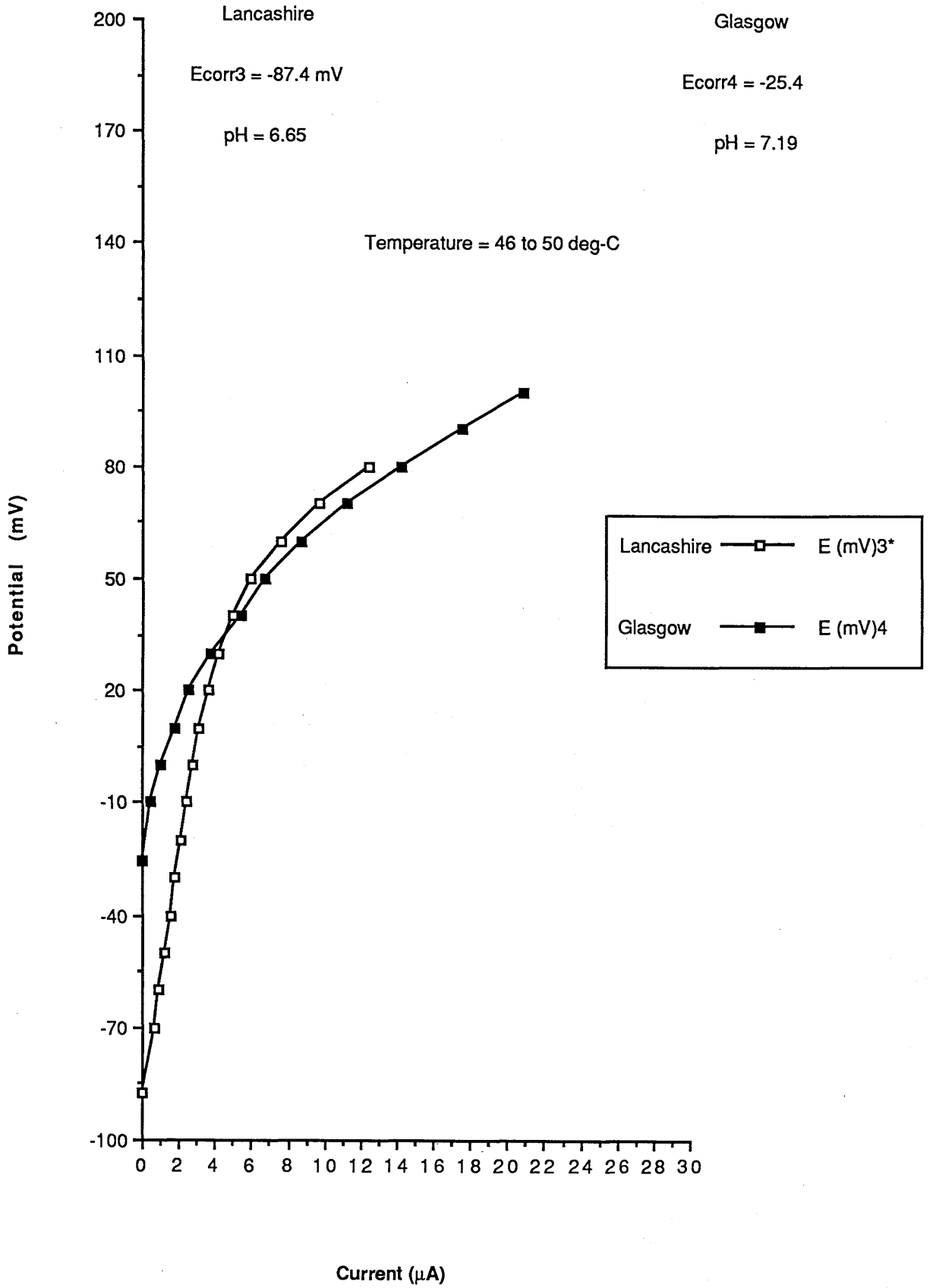
Trend in potential with respect to abrasion for both grades of copper.



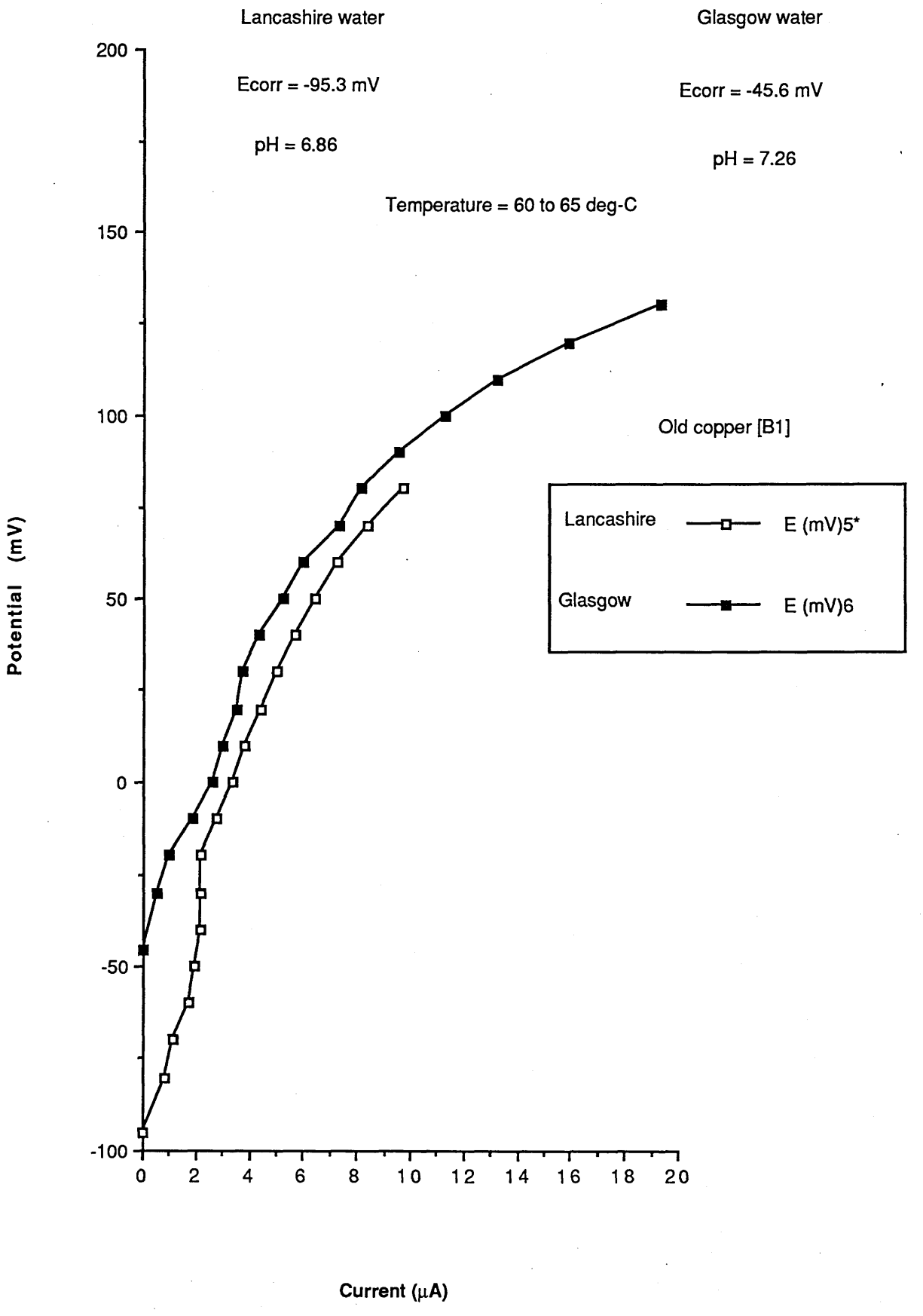
Glasgow water vs Lancashire water Figure 50



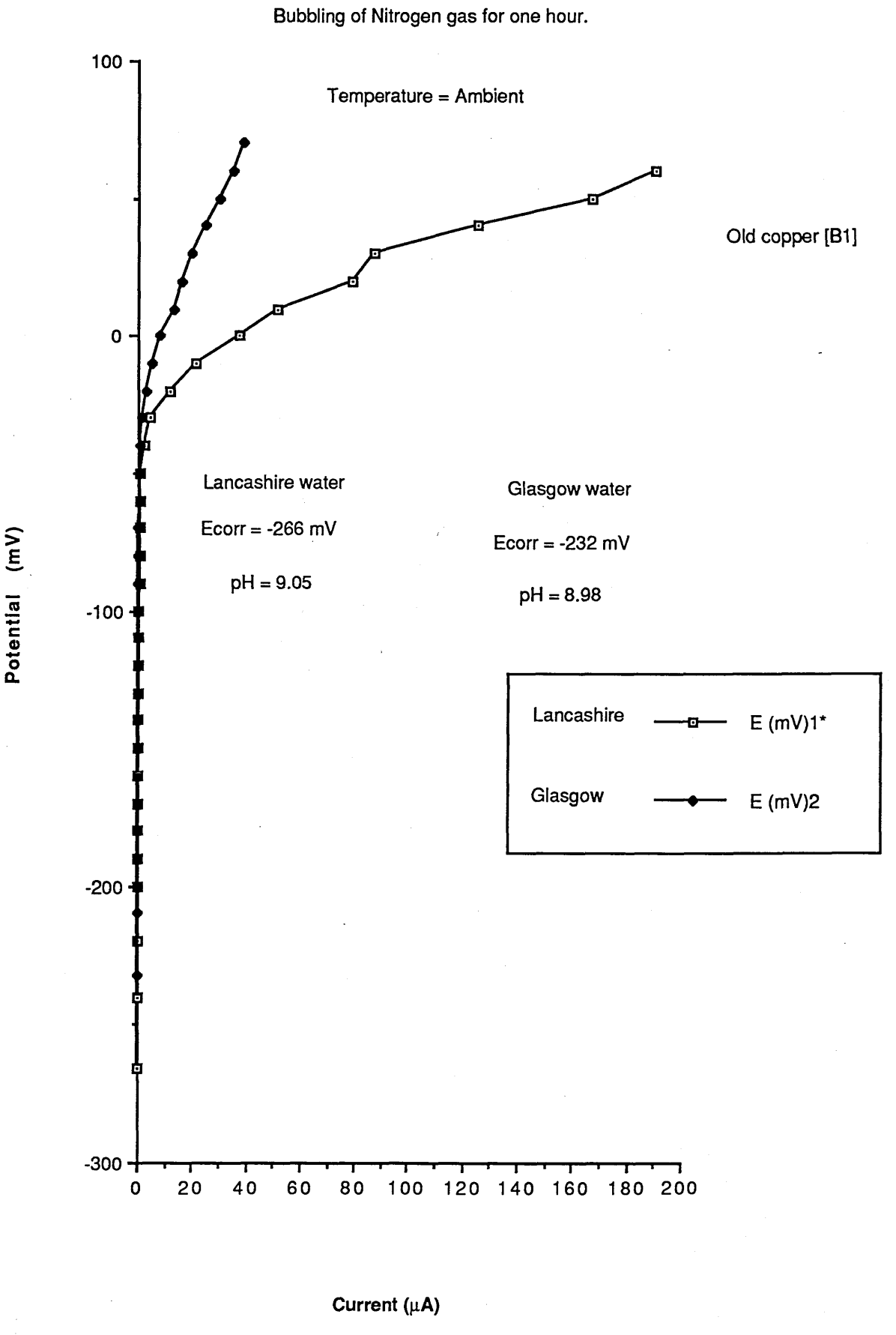
Glasgow water vs Lancashire water Figure 51



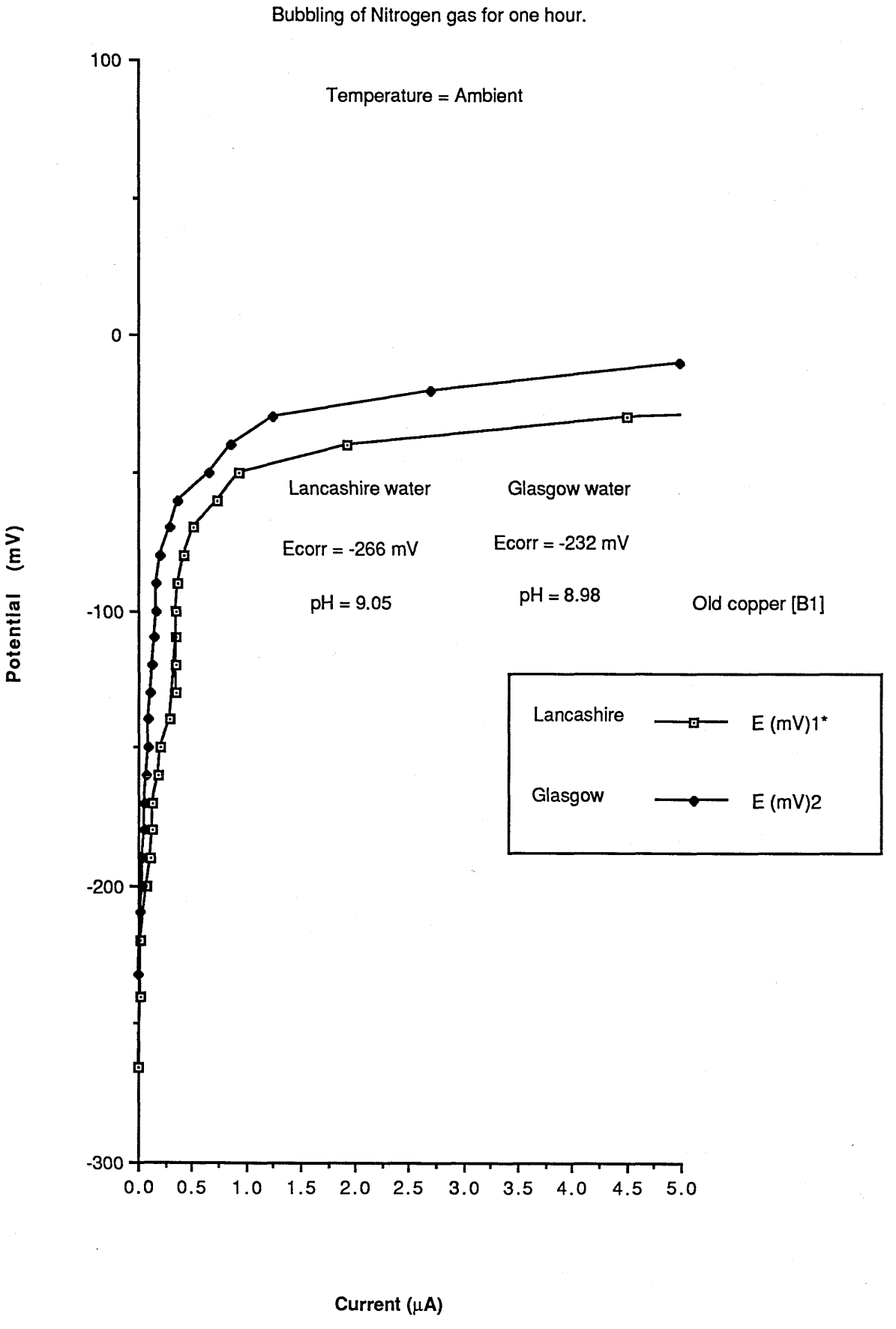
Glasgow water vs Lancashire water Figure 52



Glasgow water vs Lancashire water Figure 53

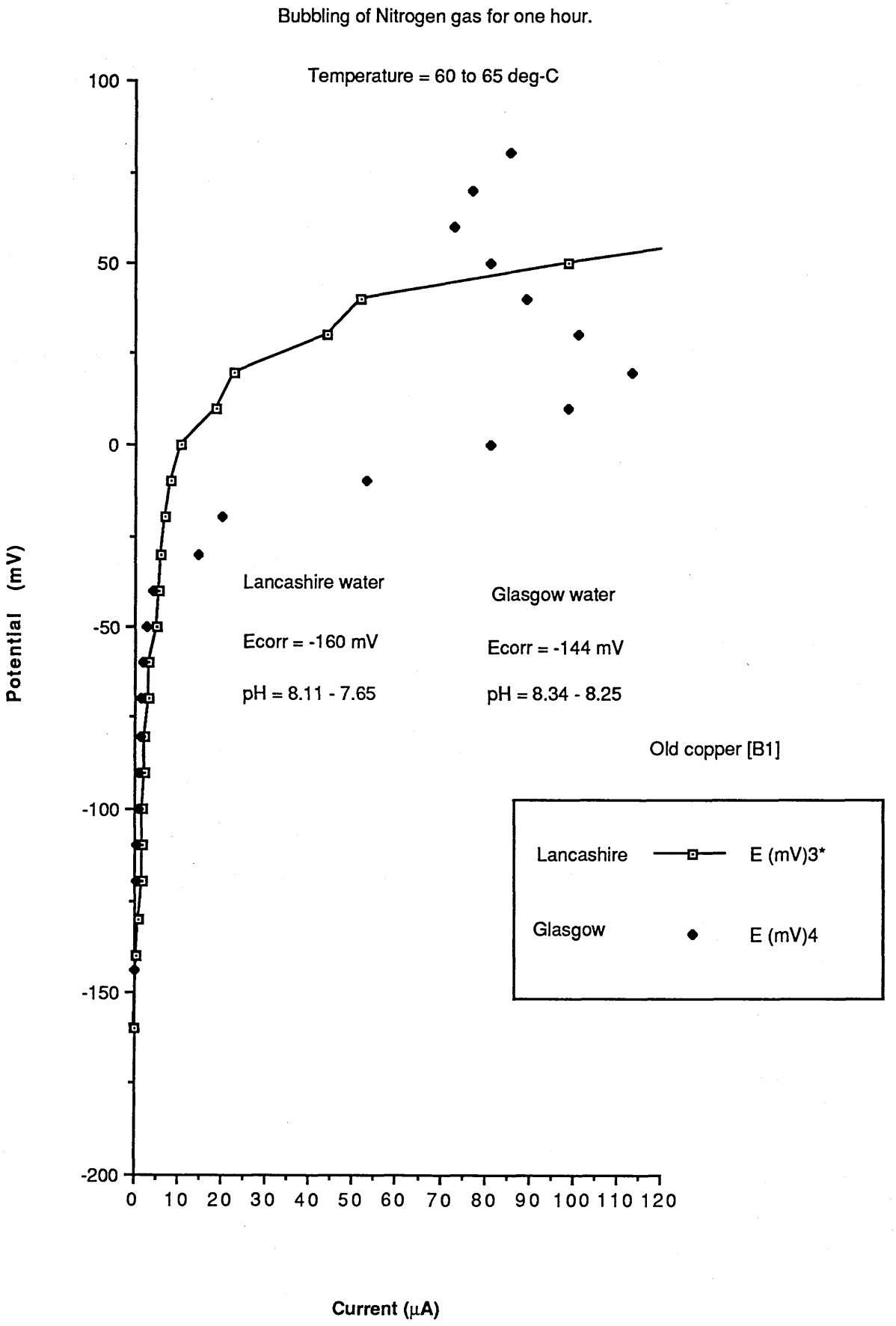


Glasgow water vs Lancashire water Figure 53A



Glasgow water vs Lancashire water

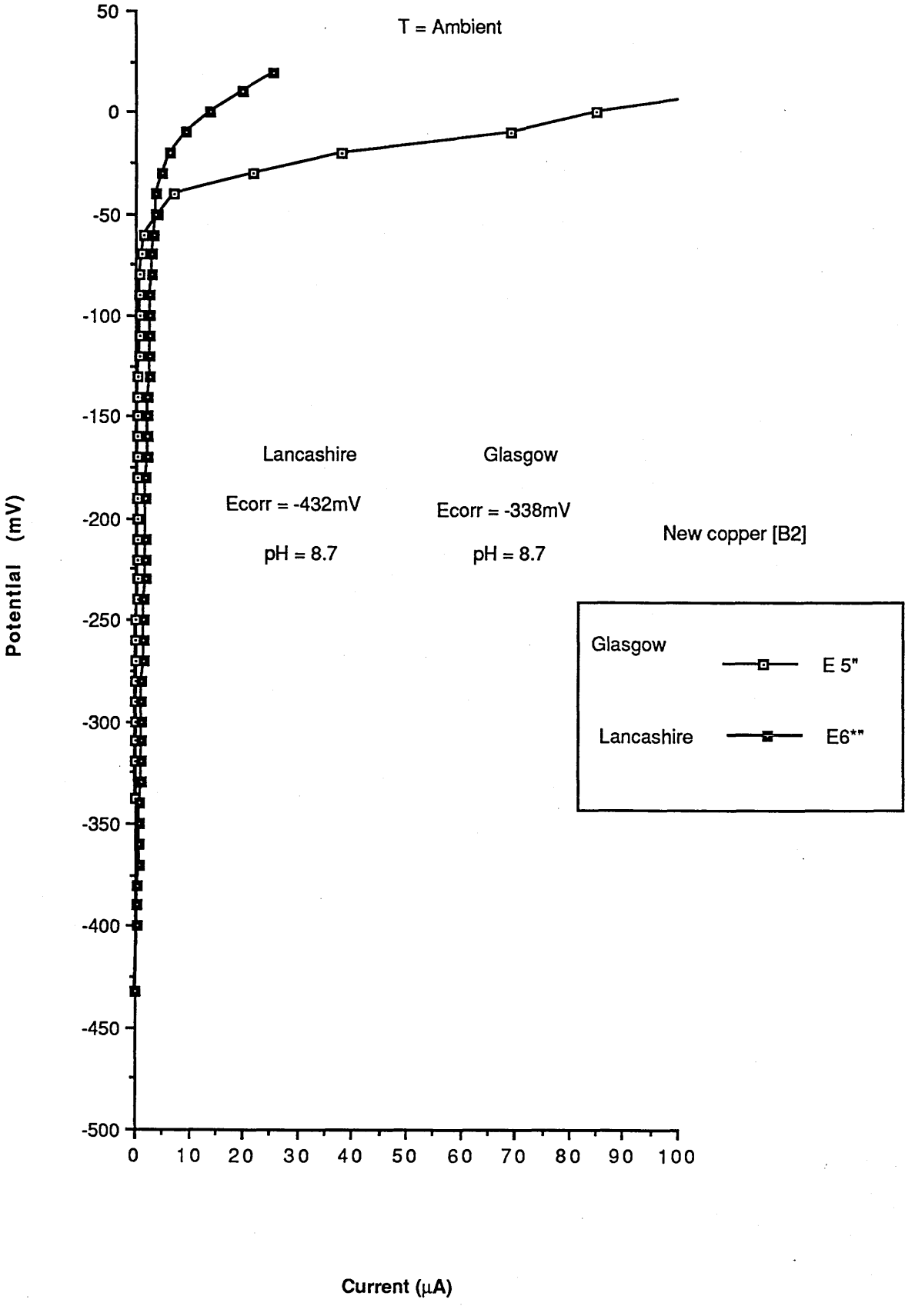
Figure 54



Glasgow water vs Lancashire water

Figure 55

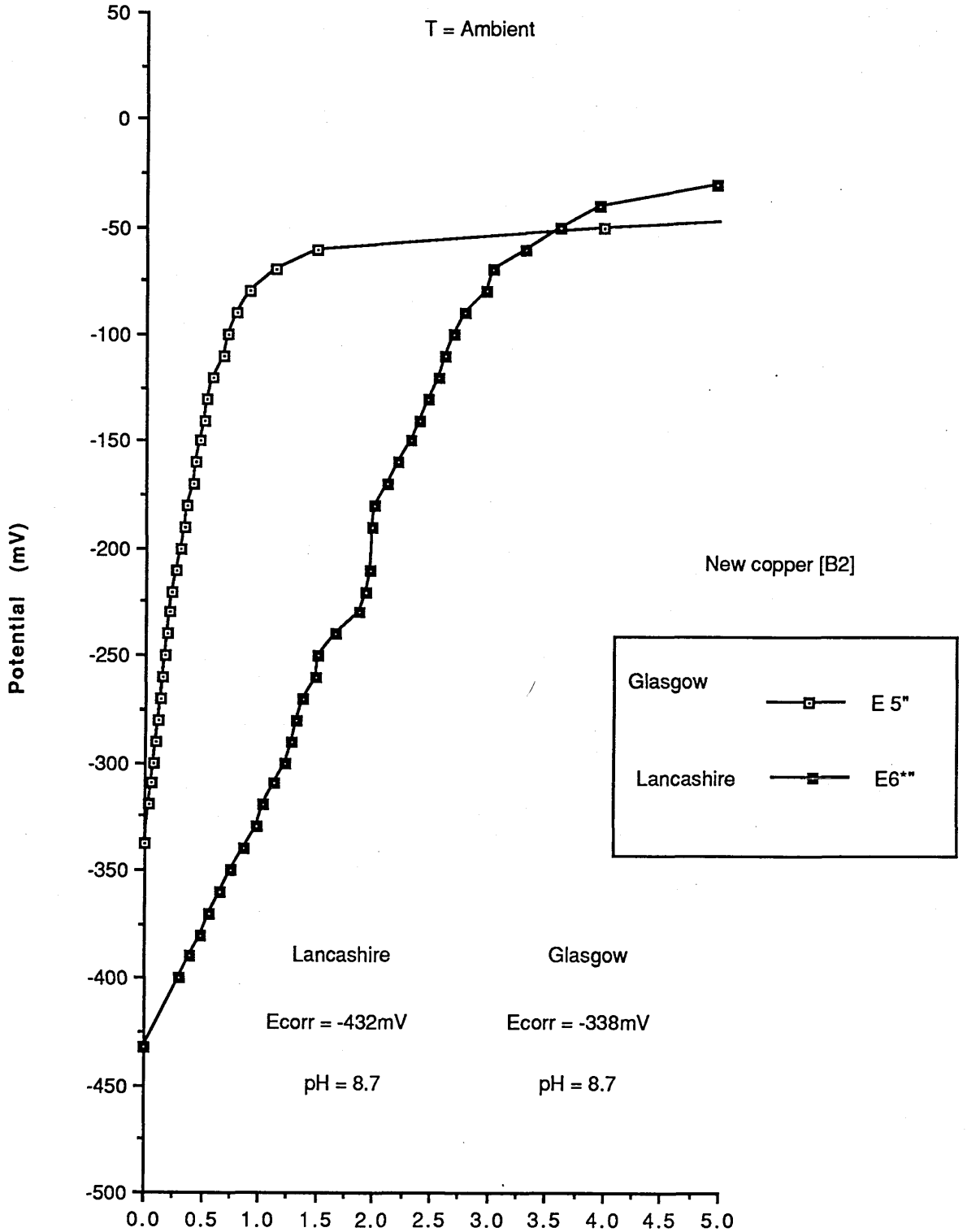
Bubbling of Nitrogen gas for one hour.



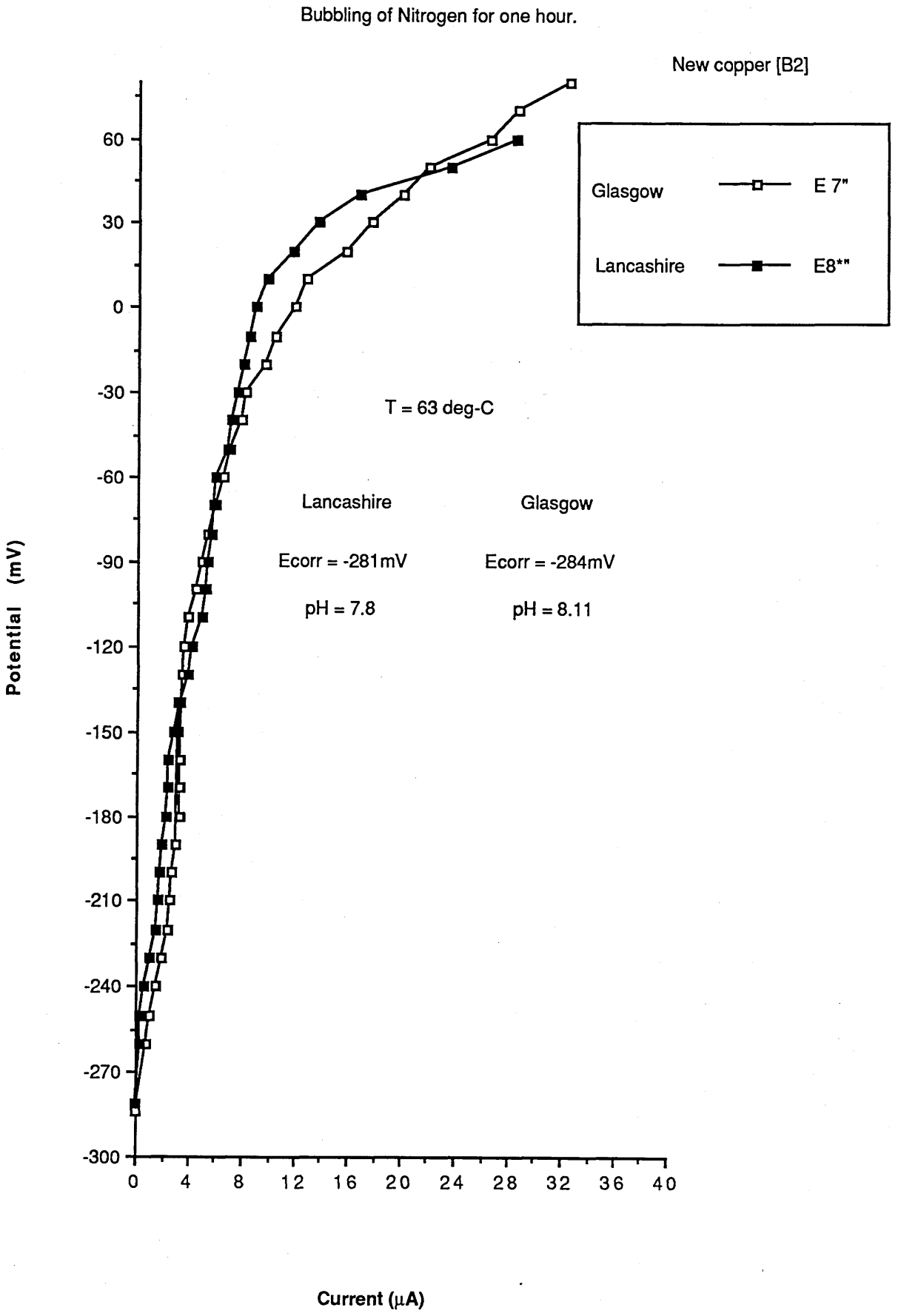
Glasgow water vs Lancashire water

Figure 55A

Bubbling of Nitrogen gas for one hour.

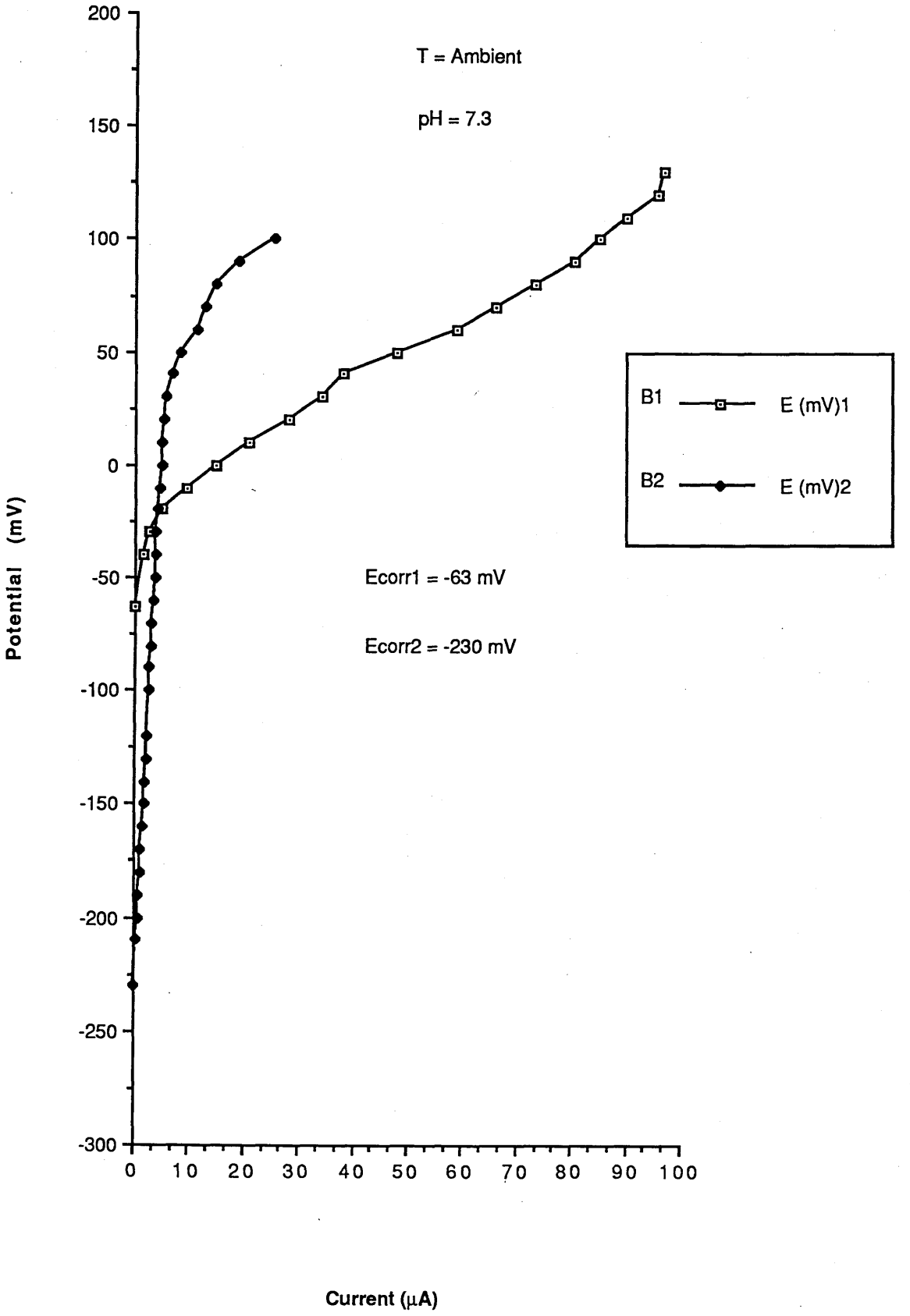


Glasgow water vs Lancashire water Figure 56



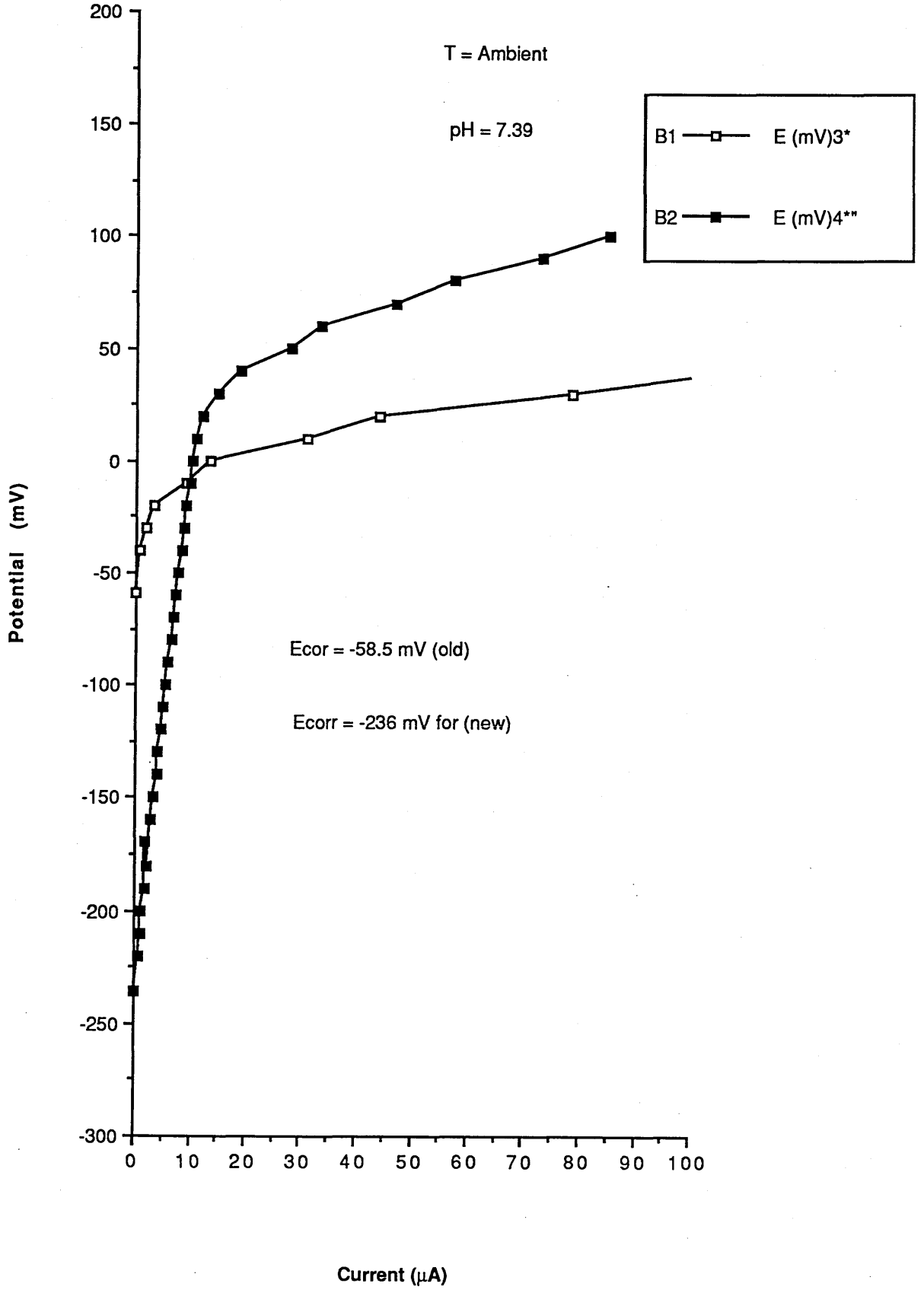
GLASGOW WATER Figure 57

Oxygen gas bubbled for one hour.



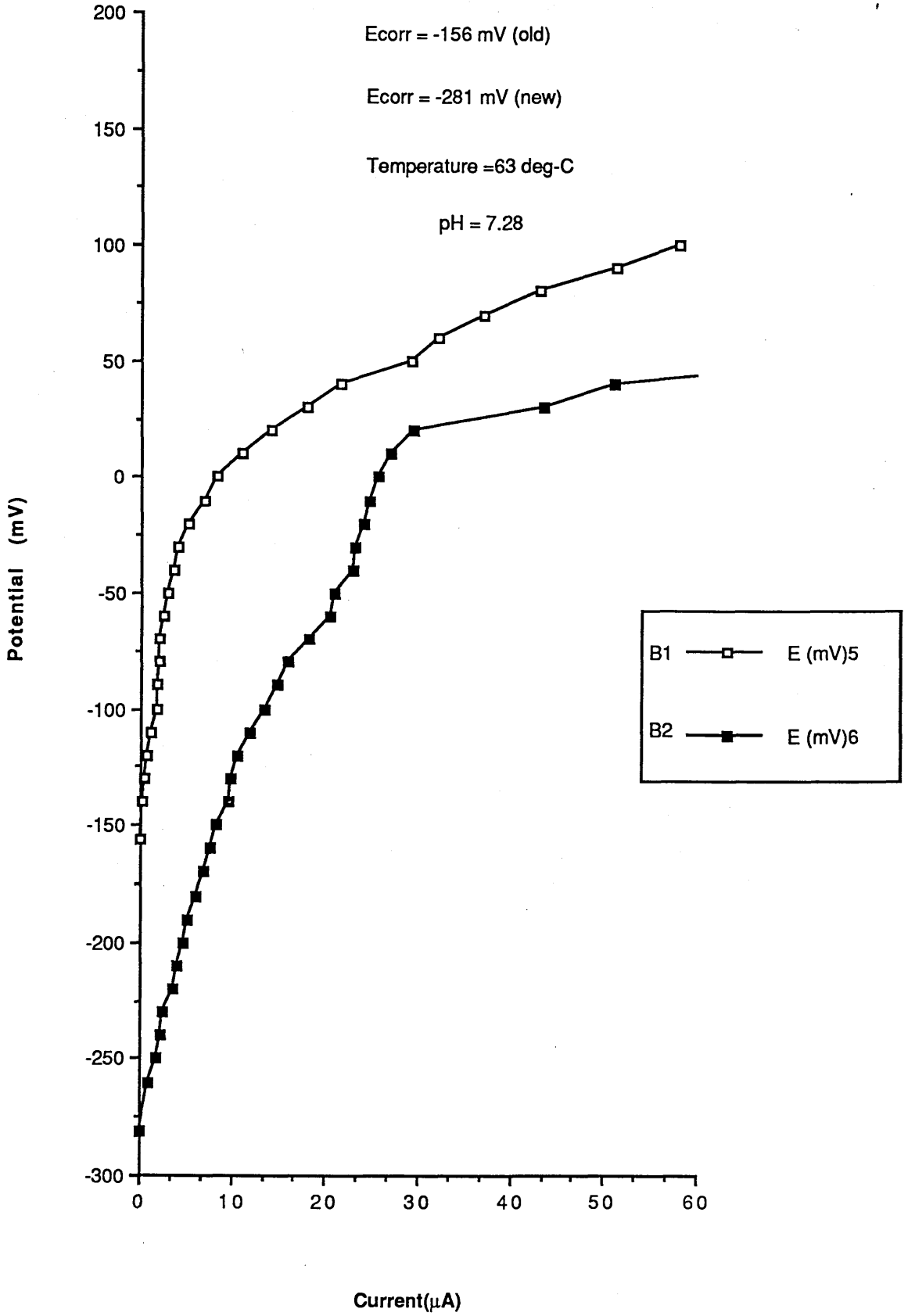
LANCASHIRE WATER Figure 58

Oxygen gas was bubbled for one hour.



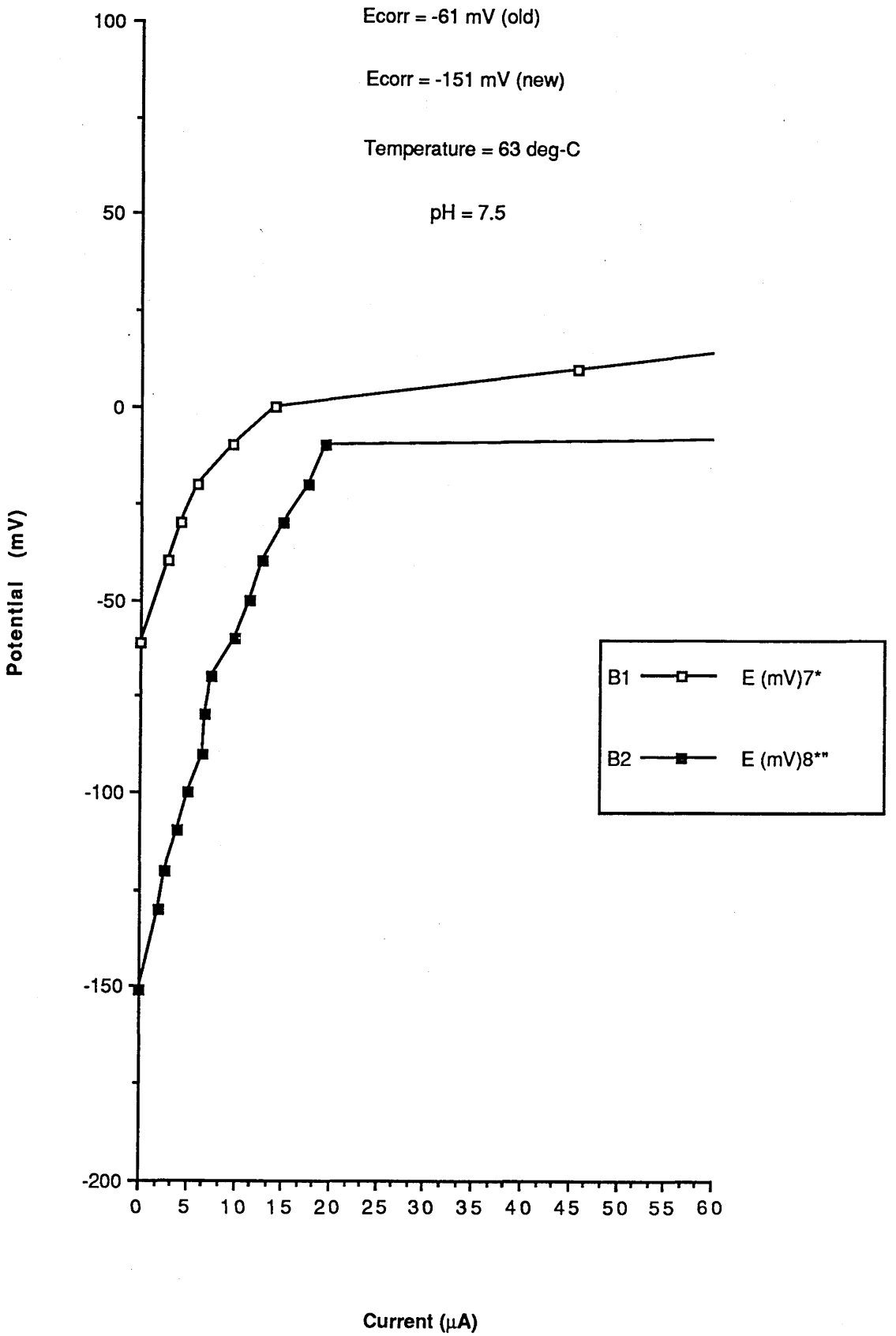
GLASGOW WATER Figure 59

Bubbling of oxygen for one hour.



LANCASHIRE WATER Figure 60

Oxygen gas was bubbled for one hour.



CHAPTER V

GENERAL DISCUSSION AND CONCLUSIONS

5.1.1. GENERAL DISCUSSION

The electrochemical corrosion behaviour of several grades of copper in Glasgow tapwater was studied under different conditions.

It was found that in stagnant condition the copper specimens attain more noble potential as compared to moving cold water (figure 1&4). This noble potential behaviour of the copper specimens upon immersion in stagnant water may be related to the reaction of different species present in the water and perhaps these reactions effect the electrode potential of copper specimens more easily in stagnant condition as compared to moving cold water. This may well be related to the action of carbon dioxide because of the lower pH values observed in the stagnant condition as compared to moving cold water. The decline in pH of Glasgow tapwater has been reported by Watker (23). She suggest that the presence of humic acid in the water distribution system may also be responsible for such decrease in the pH. It is also possible that chelation have some effect on the electrode potential of copper specimens if there is humic acid present in the water. As the pH of water in the distribution system declines, it will become more acidic and will increase the cuprosolvent action. The pH has great influence on the tendency of a water to affect its stability of protective coating.

This parameter may be an important objective, particularly in large and complex installations, is to avoid, where possible pipe runs and where stagnant and semi- stagnant conditions exists for long periods.

In slowly moving cold water the copper specimens appear to develop a protective film and may indicate satisfactory performance of copper in this situation for the period of time involved in this work.

As it has been mentioned earlier that in moving cold water the experiments were performed in two different conditions. This was done in the hope to study and collect some information on the surface layer existing on the specimens. This work has not been performed systematically but the aim behind illumination work carried out so far here was to see if there is such sudden drop in potential as was observed by other investigators (17,36) because they have attributed the sudden drop in potential to the presence of cuprous chloride in the corrosion product. The cuprous chloride is an n-type semi-conductor and produce negative drop in potential under illumination. The effect of illumination has been observed on the developed surface layer because of the sudden drop in potential time curve for old copper specimen and may suggest the presence of cuprous chloride in the surface layer.

The second thing was the positive drift in free corrosion of the specimens with the length of time which might be due to the presence of cuprous oxide on the surface of the specimens.

On visual examination under low power microscope a uniform green/brown deposit was observed on the surface of copper specimens exposed to cold water condition which may be associated with the development of corrosion products and/or deposits setting on surface and might imply a gradual drift towards conditions in which pit initiation will eventually occur. Consequently, the observation in this study mightly imply an incident of pitting attack in this water at times in occur of the one year experiments undertaken herein. However other factors, associated with practical cold water distribution system and not considered due to time constraints in this work, may be involved in the observed practical corrosion of cold water pitting.

These include, flow conditions, residence time in storage and pipe systems and commissioning practices etc.

The presence of corrosion product on the surface of the specimens may also be conceived (table 1, moving cold water) due to which somewhat more positive breakdown potential values were observed after long exposure time (3 &12 months) as compared to short exposure time (1&6 days).

The first item is to note that these laboratory experiments were carried out on square specimens ($10mm^2$) in order to get some information on the relevent conditions occuring in the actual water distribution system. This experimental work describes a simple arrangement with sufficiently slow flow rate while in water distribution system and especially in large buildings the water system are extremely complex because of the length of pipe installed and different flow conditions.

In water distribution system problem can arise due to excessive water velocity which remove the existing surface layer in extreme conditions and can cause premature failure by erosion/corrosion and or cavitation damage. This problem may be avoided by the proper system design and operation of the water distribution sysem.

In slowly moving hot water (40-50^{o}C) and in more-rapidly flowing hot water (29-48^{o}C), similar protective film behaviour was observed which indicate that the performance of of copper may be satisfactory in this condition due to the presence of such protective layer observed on the surface of the specimens.

A black corrosion product layer was observed underneath the powdery deposit in moving hot water which may be due to the rise in temperature as compared to cold water and also suggests that some changes may takes place in the corrosion product layer with response to temperature.

The different behaviour observed for the same grade of copper may be due to the difference in the exposed conditions in both places. This part of work provide an indication on the sensitivity of copper to its initial treatment and perhaps the handling, storage and poor workmanship may also have a great influence on the performance of copper.

In hot water at 60^{o}C, the corrosion behaviour of copper specimens was much more complex. The specimens exhibit clearly active behaviour upon initial exposure and appearing to remain so for period upto one year.

The corrosion product observed on the specimens was generally rather similar in appearence to that found in normal hot water at 40-50°C, a black corrosion product layer was observed underneath the powdery deposit. The E/c results imply that such a corrosion product does not contribute a normal passive film at 60°C. It does afford some degree of protection especially in longer term as low corrosion rates shown. This lack of complete protection is substantialated by visual observation of pits on unpolarised specimens after exposure for one year (photograph1H, 2H).

Moreover, given the similarity of the corrosion product/deposits at 40-50° to 60°C, it might be speculated that local attack at the lower temperature might be initiated at longer exposures than undertaken in this study.

In hot water at 60°C, the corrosion product was providing some protection in the sense that low corrosion rate, especially in the first few days were observed and not by the classic passive film mechanism observed at lower temperatures.

These results and the visual evidence of the onset of localised pitting in hot water at 60°C suggest that the performance of copper is less satisfactory in this condition.

The increase in current with the rise in temperature was observed in the potential holding work which may be the reason for the corrosion of copper in this locality. The second thing was that different free corrosion potential values were observed after grinding each time for the same copper specimens which may suggest the variation in the composition of copper with thickness.

This work has provided a good basis of understanding of the behaviour of copper in water of this locality.

It was found that copper specimens attain more noble potential upon immersion in Glasgow water as compared to Lancashire water. It was also noticed that in deaerated water the specimens shows more negative free corrosion potential behaviour as compared to aerated condition. The higher pH values was observed in deaerated water as compared to aerated water. The above two factors may be responsible for the observed large breakdown potential range in the deaerated condition as compared to aerated condition.

5.2.1. CONCLUSIONS

The following conclusions can be drawn from the above described experimental work.

I: Stagnation of water may be avoided in the copper tube because of the decrease in pH which stimulate the cuprosolvent action.

II: There was a natural positive drift with time in free corrosion potential towards values of potentials at which film breakdown occurs in all conditions.

III: In moving cold water, passive behaviour was observed for different grades of copper after one year of immersion and suggest satisfactory performance under this condition.

IV: In normal hot water (40-50^{o}), similar protective film behaviour was observed for different grades of copper after 11 months of immersion and also suggest satisfactory performance in this condition for the period involved in this study.

V: In hot water at 60^{o}C, no passive behaviour was observed for copper specimens for the period involved in this work (one year) and suggest less satisfactory performance of copper under this condtion.

VI: The difference in corrosion product layer observed in different conditions suggest some changes which is occuring in the properties of the corrosion product at higher temperatures.

VII: The different behaviour observed for the same grade of copper obtained from different merchants suggest its sensitivity to initial treatment.

VIII: The different values of Ecorr observed for the same grade of copper each time after grinding suggest the variation in composition of copper with thickness.

IX: The noble free corrosion potential values was observed for the copper specimens in the aerated condition as compared to deaerated condition which suggest the influence of aeration on the performance of copper.

5.3.1 Future recomendations

The results in this work have provided a sound foundation regarding the E/c aspect of corrosion behaviour of copper in local water. The results, taken togther with the visual observations, provide some points towards tentative explanation of practical problem associated in this region (especially at higher temperatures) but also indicate topics on which future work might usefully be carried out.

a: A closer investigation of the length of time exposed to stagnant water. This would simulate the effects of "dead legs" in a plumbing system.

b: It will be beneficial to check the pH of water supply entering buildings on regular basis. This will provide the information on the variation of pH through water distribution system.

c: The experiments are required to simulate commissioning /pre-operation factors and their effects on subsequent corrosion behaviour. This will provide some information on the influence of chlorination especially shock doses employed in the building industry.

D: Experimental programme designed to yield, detail correlation of the physical, chemical and micro biological characteristics of the corrosion product and deposits with time and have corrosion behaviour.

e: The long term experiments are required on the rapidly flowing rig which will provide more indications of the long term behaviour of copper in a real system at all temperatures.

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N.B.

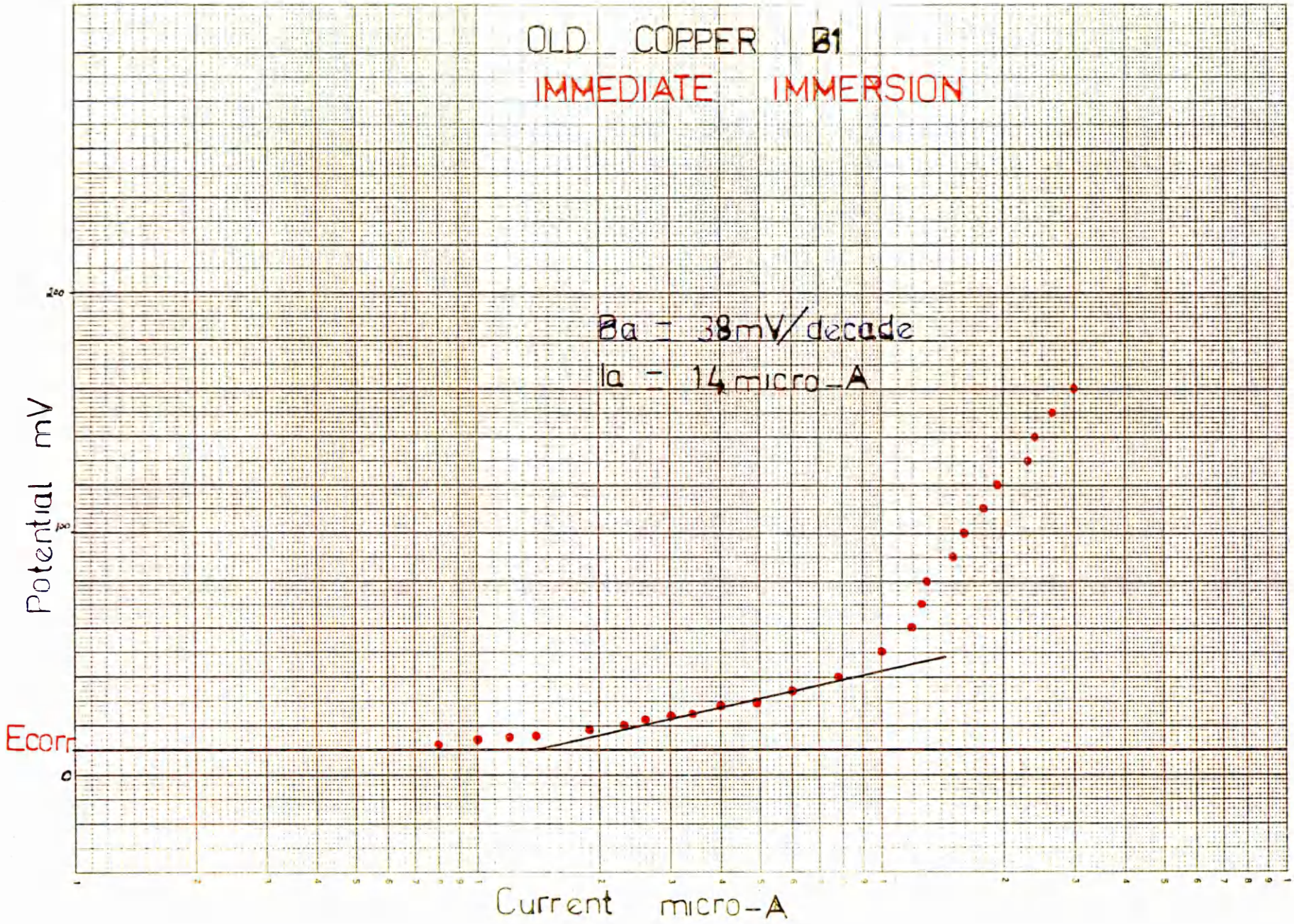
References {2,11,12,25,27} has been taken from the International Symposium on the " CORROSION OF COPPER AND ITS ALLOYS IN BUILDINGS" TOKYO, 1982, March 16-17

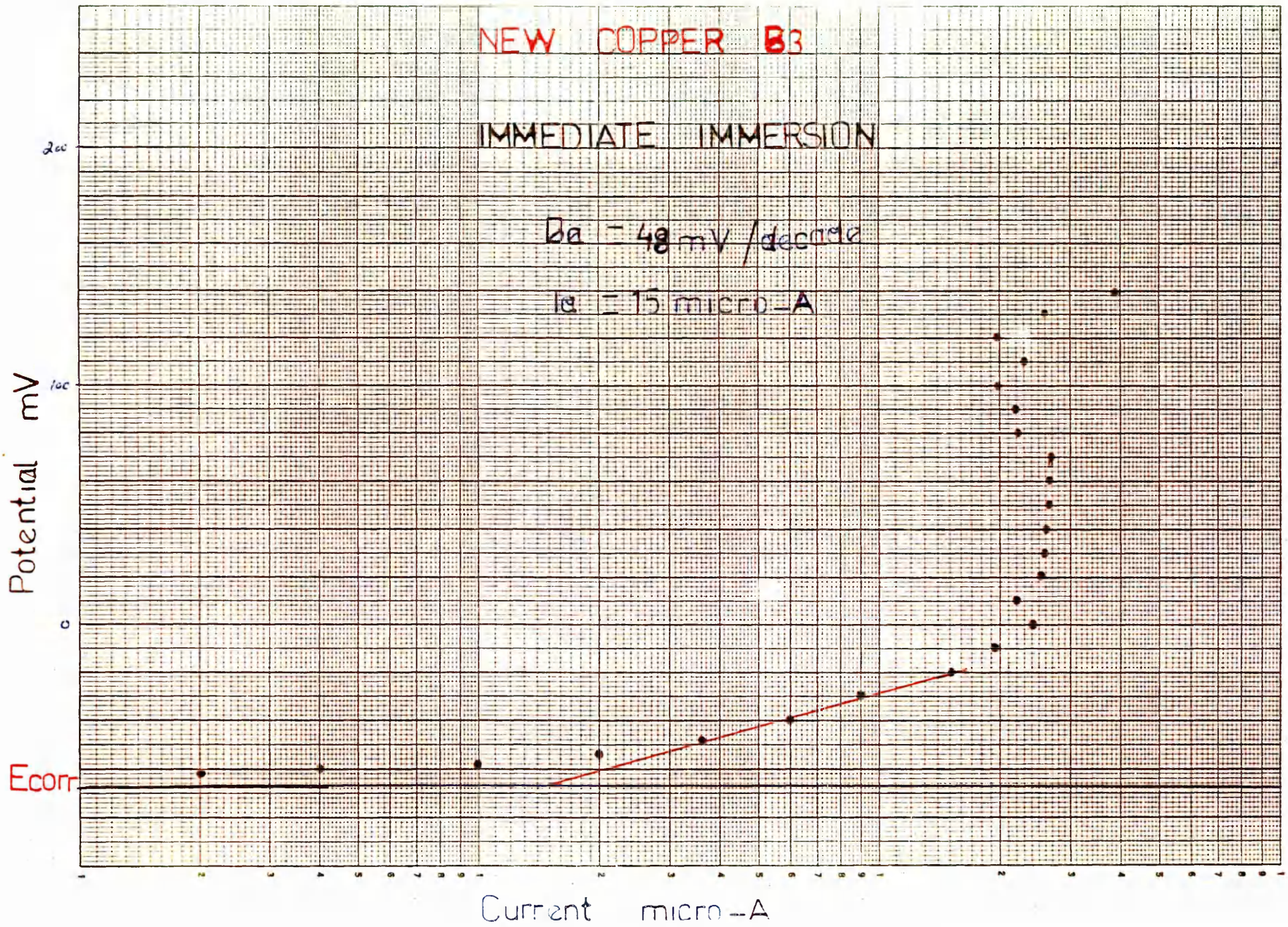
Table A: : **Analysis of major components of Glasgow tapwater.**

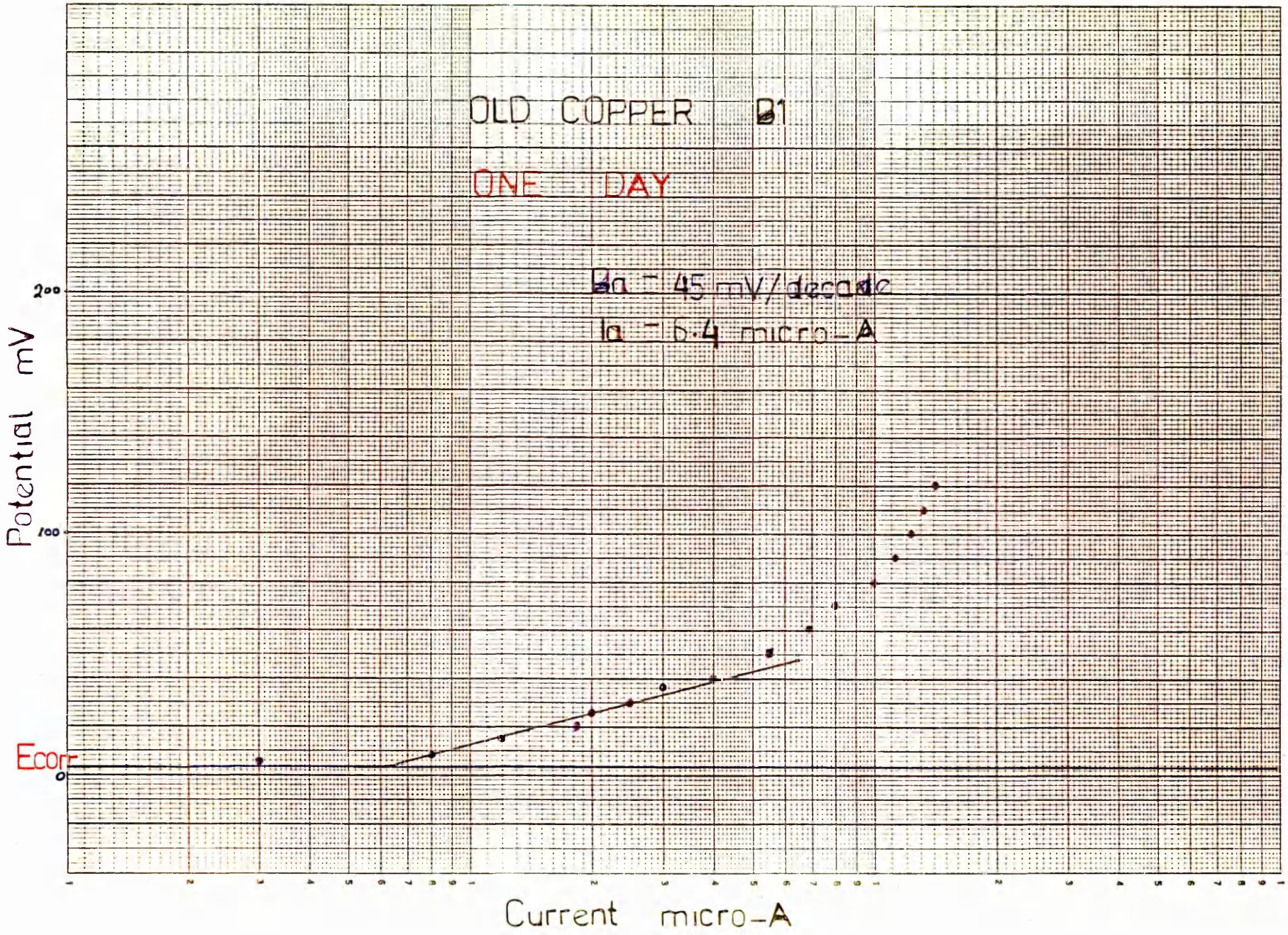
Water constituents	Concentration in ppm
Chloride	6
Sodium	4
Sulphate	5
Magnesium	7
Calcium	4
Potassium	.7
Silica	1
Aluminium	.02
Nitrate	.8
Fluoride	.01
Iron	.05
Alkalanity	18.3 {bi-carbonate} 15 as Calcium carbonte
Conductivity	45 µs/cm
pH	7-8.5

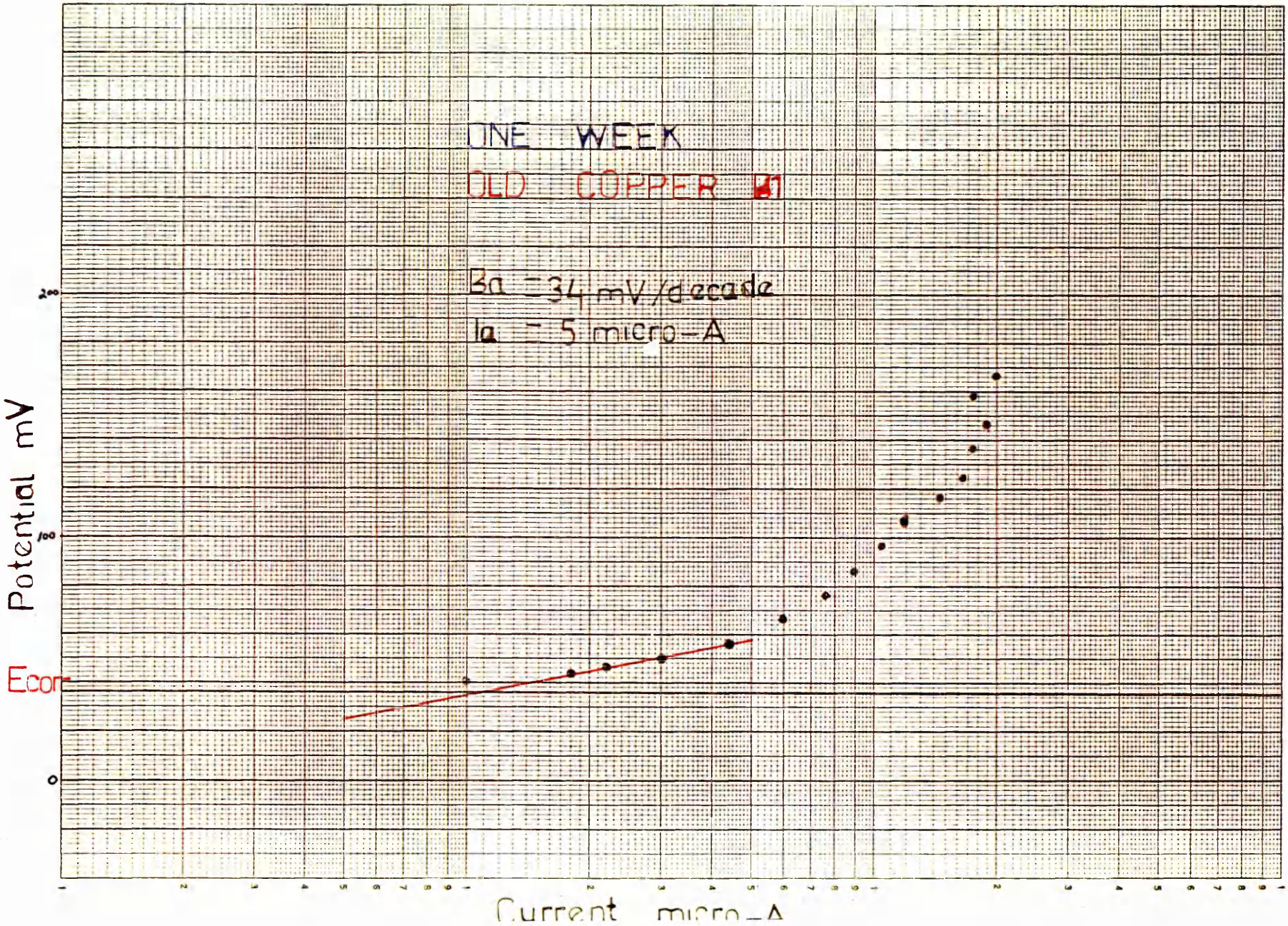
LANCASHIRE WATER

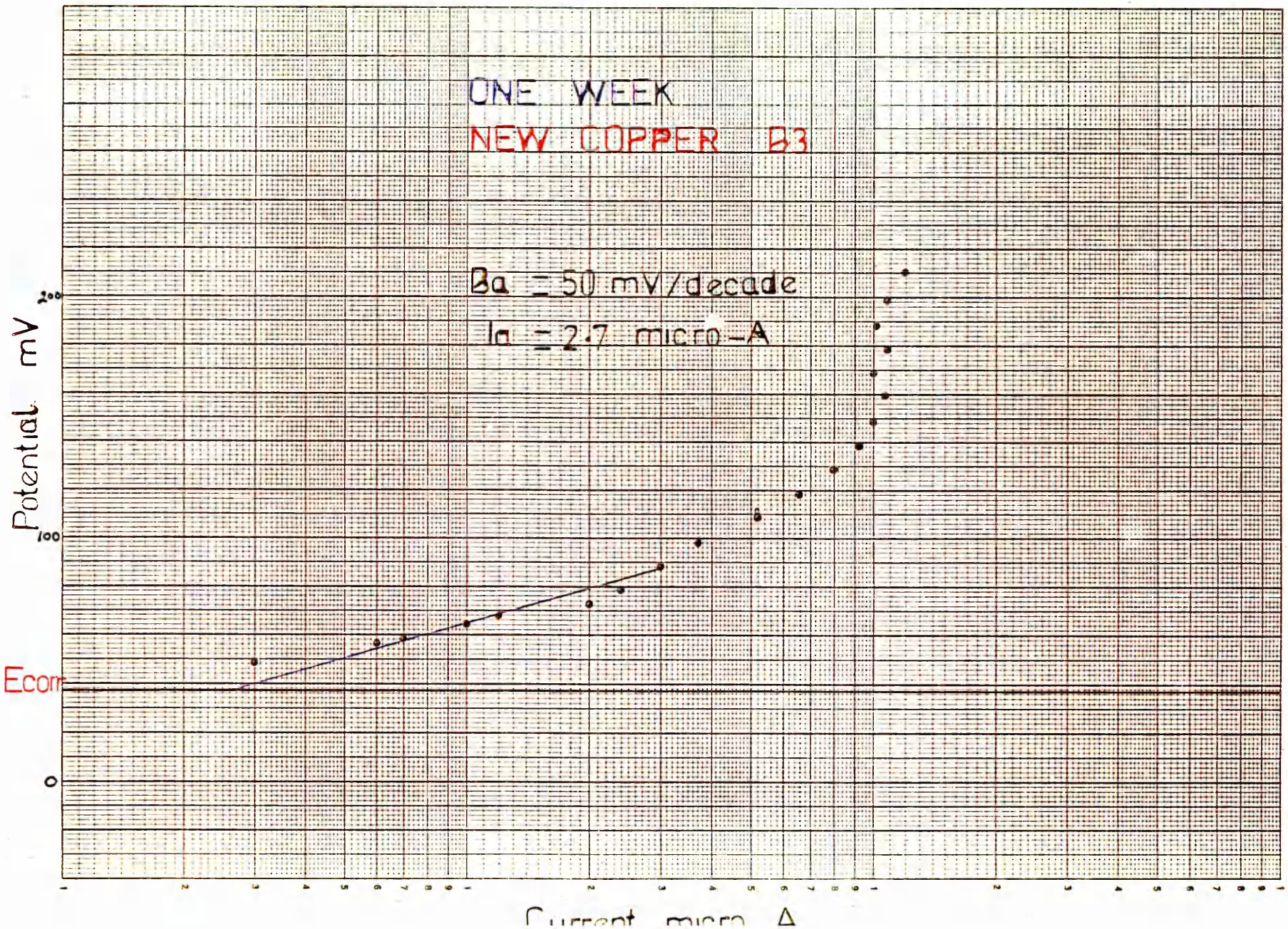
Conductivity = 129 µs/cm
Dissolved Oxygen = 7.5 p.p.m.
Temperature = Ambient.

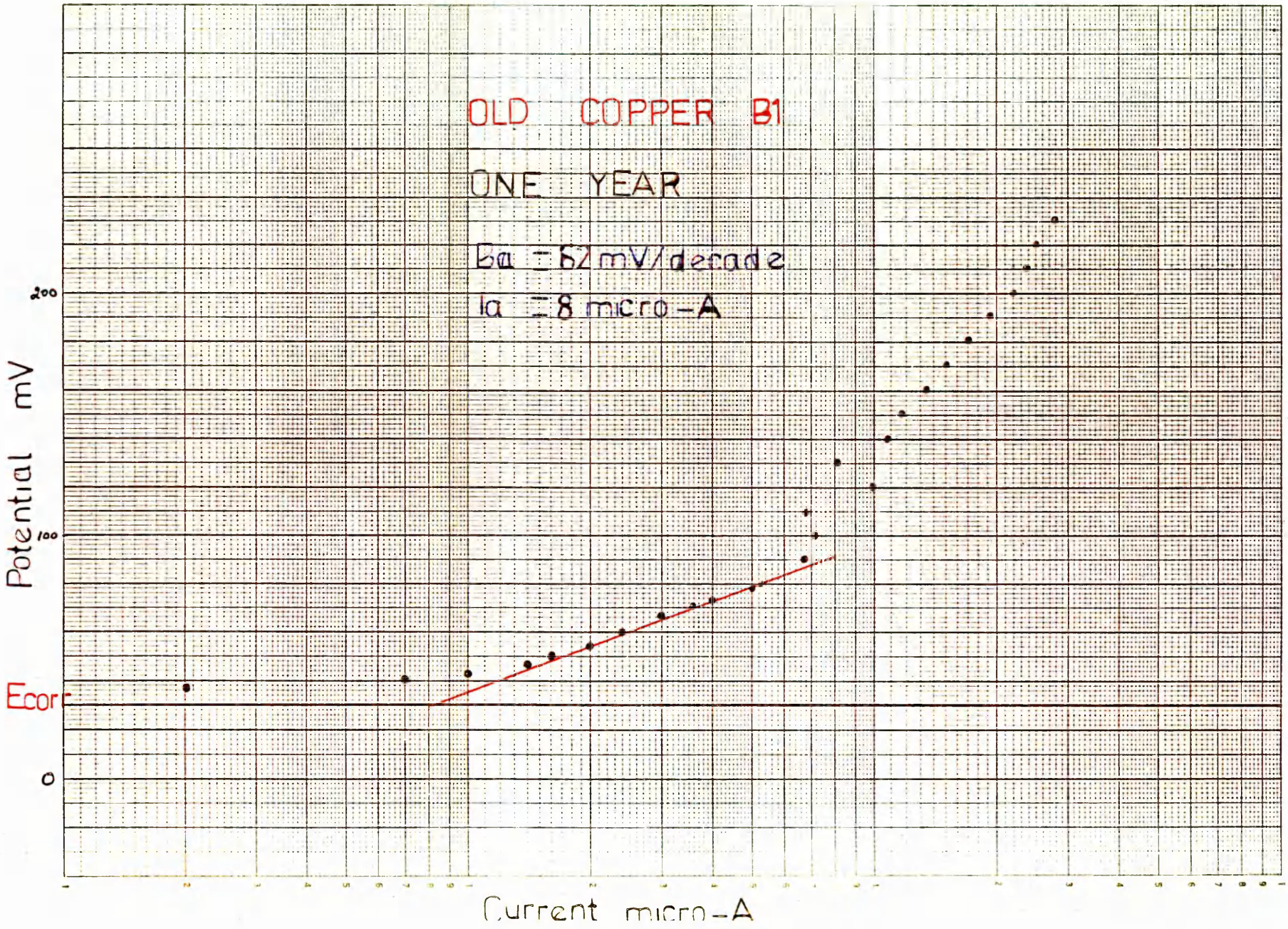

OLD COPPER B1
IMMEDIATE IMMERSION
Ba = 38mV/decade
Ia = 14 micro-A
200
100
Potential mV
Ecorr
0
Current micro-A


NEW COPPER B3
IMMEDIATE IMMERSION
Ba = 48 mV / decade
Ia = 15 micro-A
Potential mV
200
100
0
Ecorr
Current micro-A


OLD COPPER B1
ONE DAY
Ba = 45 mV/decade
Ia = 6.4 micro-A
200
100
Potential mV
Ecorr
0
Current micro-A


LINE WEEK
OLD COPPER #1
Ba = 34 mV/decade
Ia = 5 micro-A
Potential mV
200
100
0
Ecor
Current micro_A


ONE WEEK
NEW COPPER B3
Ba = 50 mV/decade
Ia = 2.7 micro-A
Potential mV
200
100
0
Ecorr
Current micro A


OLD COPPER B1
ONE YEAR
ba = 62 mV/decade
Ia = 8 micro-A
200
100
0
Potential mV
Ecorr
Current micro-A